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GEORGE C. LLOYD

SECRETARY

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# IRON-CARBON-SILICON ALLOYS.[1]

By J. H. ANDREW, M.Sc. (Manchester).

The literature of the iron-carbon-silicon alloys is so extensive that the author does not propose to go into detail, or even summarise the work of previous investigators, but rather to discuss generally the work of others directly bearing upon this paper.

It has for many years been known that the addition of silicon to cast iron has the immediate effect of increasing the graphitic content of the iron at the expense of the combined carbon; little is known, however, as to the actual mechanism of this action.

One of the ablest papers published on this subject is by Dr. Stead,[2] in which he reaches the following conclusions:—

3. The evidence appears to support the view long held by some, and more recently accepted by others, that during the freezing of iron-carbon hypo-eutectic alloys, after the crystallisation of the primary austenite, and in the eutectic and hyper-eutectic alloys, it is the carbide and not graphite which primarily forms, and that the carbide afterwards decomposes into graphite and austenite.

4. It has been proved by chemical methods that when the hypo-eutectic alloys low in silicon freeze, nearly all the silicon crystallises out with the primary austenite, and it follows that in gradually increasing the carbon so as to reduce the quantity of primary austenite, the silicon remaining constant, the austenite which is so formed must be gradually enriched in silicon up to saturation point, and that when that point is reached the excess silicon crystallises out with a portion of the carbide of iron to form carbo-silicide of iron.

Other elements remaining constant, the same result must follow in gradually increasing the silicon.

---

[1] Report received March 3, 1915.

[2] Dr. J. E. Stead, *British Association Reports*, 1910.

5. In the alloys of eutectic proportion and in the hyper-eutectic alloys, as no primary austenite can form the silicon crystallises primarily with the carbide.

7. In Cleveland irons, which become grey on cooling and in which there is no primary austenite, the same iron-carbon phosphorus eutectic is the only eutectic to form during cooling, and instead of the ternary iron-carbon-silicon eutectic, two independent cementites crystallise, one a silico-carbide and the other carbide of iron, possibly containing a little silicide in solid solution. The micro-examination of the cold alloys, to which a little sulphur has previously been added when the metals were melted, led to the conclusion that it is the carbo-silico cementite which primarily crystallises.

8. There is evidence that the primary carbo-silicides are exceedingly unstable, and are the first to decompose into graphite and silico-austenite.

9. In the absence of any sensible quantity of phosphorus two cementites form—one the silico-carbide cementite, the other the carbide-cementite—and crystallise together as an eutectic mixture.

10. The exact composition of the two cementites has not yet been determined, as no chemical method has been found for their isolation.

11. It is evident that it is the exceedingly unstable character of the silico-carbides which is responsible for the greyness of commercial metals rich in silicon and low in sulphur.

12. Silicide of iron, when heated to 1000° C. with pure white iron free from silicon, effects the decomposition of the carbide of the white iron.

Based on this observation the hypothesis seems justifiable in cases where all the silicon present in hypo-eutectic alloys crystallises out with the primary austenite, that, after the carbide has solidified, diffusion of the silicide follows, and this leads to the decomposition of the carbide of iron into graphite and iron. In conclusion, Stead remarks that there are still many gaps to be filled, and that he hopes that others will follow up the research.

The year following this paper, Gontermann[1] published in the *Journal of the Iron and Steel Institute* his work on "Iron-Silicon-Carbon Alloys," a work which he had previously published in part in the *Zeitschrift für Anorganische Chemie.* From his experimental data Gontermann constructs an equilibrium diagram of this ternary system, the constitution of these alloys, according to him, agreeing entirely with the work of Stead.

---

[1] Dr. W. Gontermann, *Journal of the Iron and Steel Institute*, 1911, No. I.

It was with the idea of throwing some further light on this problem that the present author undertook this investigation. The procedure adopted was to take a series of freezing curves of different alloys under different conditions, and to supplement these results by the micro-examination of variously treated specimens. In the first instance, two pig irons were used as a base and other alloys higher in silicon made from these by addition of silicon in the form of 95 per cent. ferro-silicon.

The alloys were melted in salamander crucibles by means of a Fletcher-Russell injector furnace, and freezing curves taken in the usual way by the potentiometer method.

The curves attained are shown in Figs. 1 to 6. No. 1 is a freezing curve of a No. 1 pig iron, having the following composition:—

| | Per Cent. |
|---|---|
| Total carbon | 3·92 |
| Graphite carbon | 3·50 |
| Combined carbon | 0·42 |
| Manganese | 0·83 |
| Phosphorus | 0·020 |
| Sulphur | 0·005 |
| Silicon | 2·450 |

It will be seen that this pig iron shows the normal points, namely, the freezing point at 1133° C. and the point at 706°.

After melting the alloy was re-analysed in order to see if there was any loss in the carbon or silicon. The analysis gave the following results:—

| | Per Cent. |
|---|---|
| Total carbon | 3·62 |
| Graphite carbon | 3·33 |
| Combined carbon | 0·29 |
| Silicon | 2·52 |

It is thus seen that the loss of carbon is comparatively slight, but there is a net gain in the silicon content.

No. 2.—This curve was taken just after the alloy had

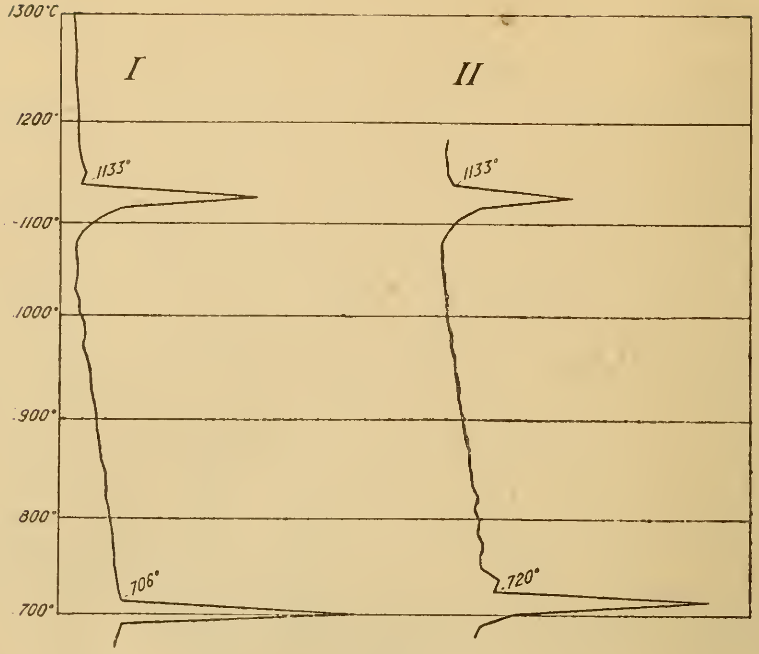
1300°C
1200°
1100°
1000°
900°
800°
700°
I
II
1133°
1133°
706°
720°

FIG. 1.

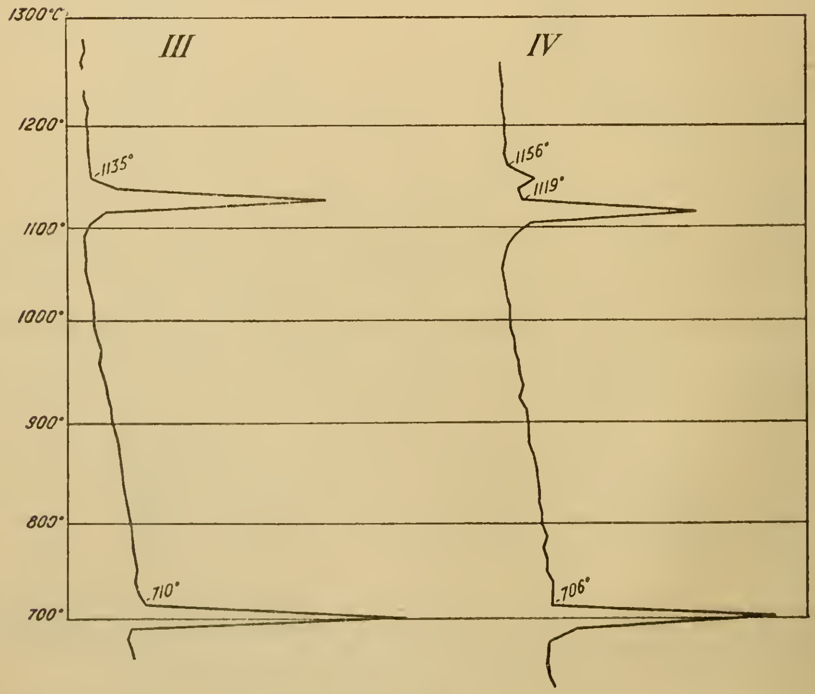
1300°C
1200°
1100°
1000°
900°
800°
700°
III
IV
1135°
1156°
1119°
710°
706°

FIG. 2.

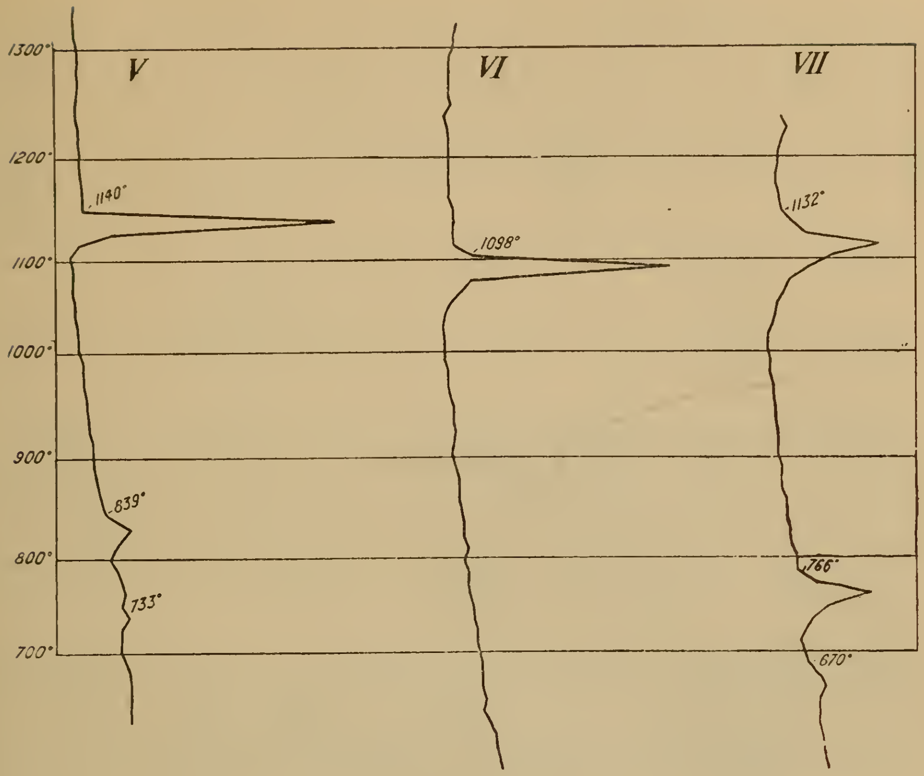
1300°
1200°
1100°
1000°
900°
800°
700°
V
VI
VII
1140°
1098°
1132°
839°
733°
766°
670°

Fig. 3.

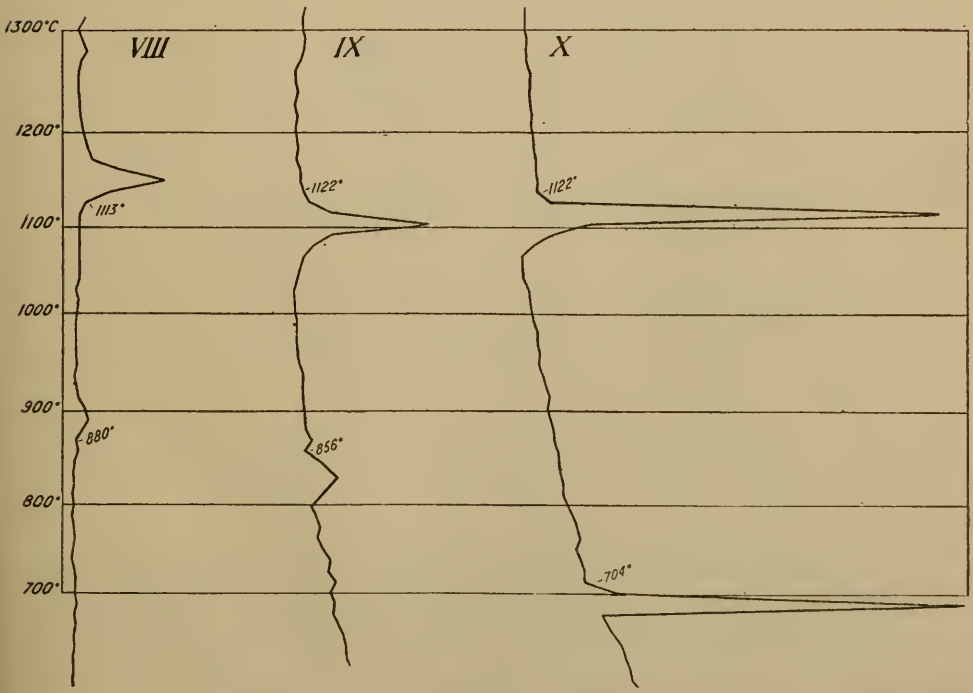
1300°C
1200°
1100°
1000°
900°
800°
700°
VIII
IX
X
1113°
1122°
1122°
880°
856°
704°

Fig. 4.

melted, being heated to a much lower temperature than the previous one, in order to see if the temperature factor played any important part in the final constitution of the alloy. The only difference to be noted, however, is in the proportion of the freezing point to the carbide change, whilst the fact of there being a small evolution of heat in No. 1 previous to the actual freezing of the alloy is perhaps also worthy of notice.

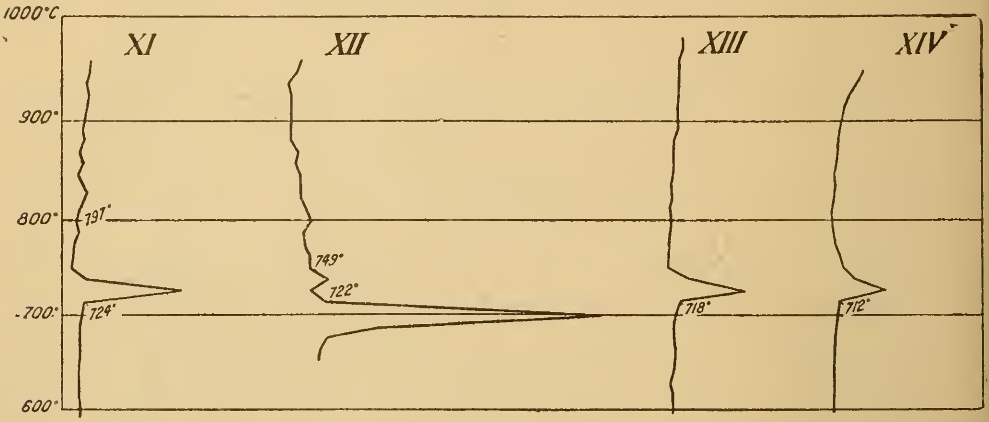

Fig. 5.

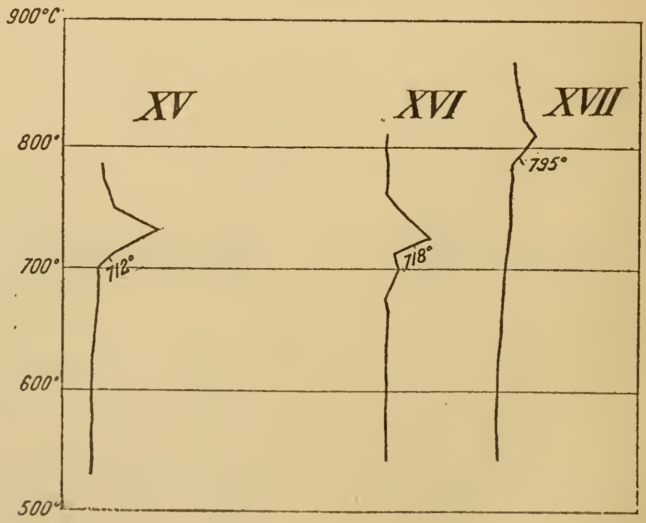

Fig. 6.

This is undoubtedly the result of heating the alloy to a higher temperature, the increased heating appearing to facilitate the formation of carbide, which, it is assumed, begins to be deposited at the temperature indicated by that point.

No. 3 is a curve of a No. 1 pig remelted after quenching so as to produce a partially white iron. The only point to be noted in this curve is that the initial freezing temperature lies slightly above the actual freezing temperature of the alloy.

An analysis of the alloy after this treatment was as follows:—

| | Per Cent. |
|---|---|
| Total carbon | 3·65 |
| Graphite carbon | 3·19 |
| Combined carbon | 0·46 |
| Silicon | 2·52 |

This analysis is rather interesting, for, although the fracture was naturally quite grey, it will be noticed that more carbon in the combined state has been retained than in the case where the alloy was not heated to a high temperature.

No. 4 is a curve of a pig iron of the following composition:—

| | Per Cent. |
|---|---|
| Total carbon | 4·03 |
| Graphite carbon | 3·41 |
| Combined carbon | 0·62 |
| Silicon | 2·29 |

Before taking this curve the alloy had previously been very efficiently quenched, so as to produce a white iron.

There are many interesting points to note. The initial freezing point now occurs at 1156° C., whilst the freezing point proper does not occur until as low a temperature as 1119°. The pearlite change takes place, moreover, at a slightly lower temperature than in the previous case. That quenching a cast iron so as to obtain a white iron, and, therefore increasing the carbide content, produces a double freezing point, is strong evidence in favour of regarding the upper point (at 1156°) as due to the separation of carbide, and also of there being no restoration of equilibrium conditions even upon melting, for, if this were so, the freezing curve of an iron, however treated, must always be the same, providing the composition be unaltered. Equilibrium appears to be restored during cooling, however, for, as has been previously seen, the analysis shows an increase of only 0·16 per cent. of combined carbon. This does not altogether agree with

Mr. Adamson's contention that a white iron remains white upon remelting, whatever the silicon content be.

No. 5 is the curve of a high silicon alloy, having the following analysis:—

| | Per Cent. |
|---|---|
| Total carbon | 3·55 |
| Combined carbon | trace |
| Silicon | 4·18 |

This curve is extremely interesting, and should be compared with curve No. 6, which is the freezing curve of an alloy containing still more silicon. The following is an analysis of this alloy:—

| | Per Cent. |
|---|---|
| Total carbon | 2·52 |
| Combined carbon | nil |
| Silicon | 9·86 |

Whereas No. 5 alloy was perfectly grey, No. 6 was quite white, and is what is known as a "glazed" iron.

Considering the two curves together, in No. 5 there are three evolutions of heat indicated—namely, the freezing point at 1140°, what appears to be the Ar3-2 point at 839°, and a very small point, the pearlite point at 733°, whereas in No. 6 there is only one point evident, namely, the freezing point at 1098°.

4·18 per cent. silicon is therefore almost sufficient entirely to eliminate the pearlite change, but the Ar3-2 point is distinctly evident, whereas when the silicon is increased to 9·86 per cent. no evolution of heat occurs below the freezing temperature.

Another remarkable point is that, whereas a small increase of silicon (3 per cent.) raises the freezing point, a larger increase produces a distinct lowering. This fact is distinctly evident in the curves of Gontermann, which show a slight maximum at 3 per cent. silicon. Whether this be due to the formation of a compound of iron and silicon, or of iron, carbon, and silicon, is not easy to determine, but as, according to Gontermann, the maximum occurs at precisely 3 per cent., whatever the carbon content, there is strong evidence in favour of the former view.

Nos. 7 and 9 are curves of a synthetic silicon alloy of which, owing to an accident, the author was unable to procure an analysis. Judging by what the alloy was intended to be, and also from the critical points upon cooling, it must contain about 3·5 per cent. silicon upon first melting (Curve No. 7) and about 4·5 per cent. silicon after remelting (Curve No. 9), the remelting affecting the combination of some further silicon on the top of the metal.

It is seen that in No. 7 there are two points, one at 670°, namely, the Ar1, and an Ar3-2 point at 766°, whilst in No. 9, containing approximately 4·5 per cent. silicon, the Ar3-2 point is raised to 856°, whilst the Ar1 is absent.

It appears, therefore, that 4·5 per cent. silicon is sufficient completely to eliminate the Ar1 point altogether.

Curve No. 8 is a heating curve taken directly after cooling Curve No. 7, and shows two points only, the Ac3-2 at 880° C. and the melting point at 1113°.

It is very noticeable, especially in the high silicon irons, that freezing continues over a wide range of temperature, judging by the shape of the freezing curves. This may be due to decomposition of the primary carbide taking place very shortly after it is deposited, the evolution of heat, started by the freezing of the alloy, being protracted by the heat evolved by this breaking up of the carbide. If this were not so, there would surely be some indication on the freezing curve at the actual temperature at which the decomposition did take place. Moreover, the fact that the melting point occurs at a lower temperature than the freezing point points to the same conclusion.

The general conclusions to be drawn from these curves are as follows:—

Heating the melt to a high temperature promotes an initial freezing point (that is to say, a double point) at a temperature slightly higher than the freezing temperature proper. The same effect is produced by quenching an iron from the liquid previous to remelting so as to produce a white iron. In view of the work of Stead and Gontermann, it is highly probable that this initial freezing point is due to the separation of either carbide of iron or carbo-silicide of iron.

The effect of adding silicon to the cast iron employed was to raise the melting point in the first instance, whilst further additions lowered it. Silicon rapidly eliminates the Ar1 point of a cast iron, 4·5 being sufficient to effect a complete elimination. The Ar3-2 point is not so readily eliminated, however, but is gradually raised in temperature as the silicon increases; indeed, there is the possibility that in the 9·86 per cent. alloy it is raised to the temperature of the freezing point, or nearly so. This would account readily for the insolubility of carbon in a high silicon alloy, the iron being in the $\alpha$ state and therefore unable to dissolve carbon. It appears from the author's experiments that Gontermann mistook the Ar3-2 point for the Ar1. With 9·86 per cent. silicon no evolutions of heat occur during cooling after freezing of the alloy. Moreover, an iron of this composition is perfectly white.

Curve No. 17 is particularly interesting. It is a heating curve of the normal pig iron, containing about 0·42 per cent. combined carbon. This curve shows no Ac1 point upon heating, and merely the Ac3-2 at 795°.

The alloy as cooled in the first instance not only showed a combined carbon content of 0·42 per cent. by analysis, but the same was clearly visible from a micro-examination. One thing is, however, clear, namely, that the carbide must have decomposed upon heating before a temperature of 700° was reached.

The silicon is not, therefore, limited in its action upon carbide of iron to higher temperatures, but must have caused the carbide to have decomposed almost spontaneously at some temperature below 700°. This remarkable and interesting fact led the author to investigate a pure iron-carbide alloy in the same way. Accordingly pure wrought iron was kept melted in contact with carbon for some little time and a freezing curve taken, the curve is No. 10.

There is an exceedingly large evolution of heat at 1122°, and a very large pearlite point at 704°, from which it will be seen that the alloy was of eutectic composition.

No. 11 is a heating curve of the same alloy taken immediately after cooling, and illustrates well the excessive smallness of the Ac1 point upon heating, indicating that a large percentage of the carbide has decomposed after being thrown out of solution.

No. 12 is a cooling curve taken immediately after heating the alloy to 1000°; it is seen that there has been considerable recombination of carbon.

Curves Nos. 13, 14, 15, 16 are heating curves taken directly after annealing the alloy at a temperature of about 600° for three days, one week, two weeks, and three weeks respectively. It will be seen that the pearlite point gradually decreases in magnitude with each successive heating. Indeed there seems little doubt that if the annealing were still further prolonged, the carbide of iron would entirely decompose and the point disappear altogether. The author hopes to continue investigations in this direction.

If the pearlite change could be made to disappear by heating below the transformation temperature, it would necessitate different equilibrium diagrams for heating and for cooling. The fact that 2·5 per cent. silicon is sufficient to decompose all the combined carbon at a temperature below 700° is strongly in favour of this interpretation, for the silicon content can be allowed for in terms of graphite, 2·5 per cent. silicon being equal to a graphite content of 1·12 per cent., thus bringing the total carbon content of the alloy to 5 per cent.

## CONCLUSIONS.

The experiments quoted indicate that carbide of iron is unstable below 700° upon cooling, breaking up extremely slowly into $\alpha$ iron and free carbon. Indeed Arnold[1] has shown repeatedly that this is the case, and that carbide of iron decomposes more quickly in a steel containing above 0·9 per cent. carbon.

In his paper before the Institution of Civil Engineers some years ago, Arnold gives two remarkable examples, referring to two steels containing respectively 1·2 and 1·47 per cent. of carbon, which, after annealing at 1000° for seventy-two hours and allowing to slowly cool, were found to contain respectively 0·28 and 1·14 per cent. of graphite. If upon allowing such a steel to slowly cool through the critical point free carbon is obtained, how much more readily will the carbide in a cast iron break up when the stable phase graphite is always present?

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[1] Dr. J. O. Arnold, *Proceedings of the Institution of Civil Engineers*, vol. cxxiii. p. 127.

That carbide of iron is stable in solution above 700° there can be no doubt, but as soon as separation of carbide occurs at 700° it immediately becomes an unstable body, and slowly transforms into carbon and *a* iron. Moreover, upon heating, solution of carbon will not take place until the temperature of the Ac3 point has been passed and the iron transformed into the $\gamma$ state. This necessitates, therefore, a different equilibrium diagram for heating, and two diagrams will thus be necessary, one showing the change of constitution during heating, and the other the change in constitution during cooling. A form of the two diagrams is given in Figs. 7 and 8 respectively; the diagram, it will be seen, follows the Ruer-Benedicks type. The most noticeable features are as follows:—

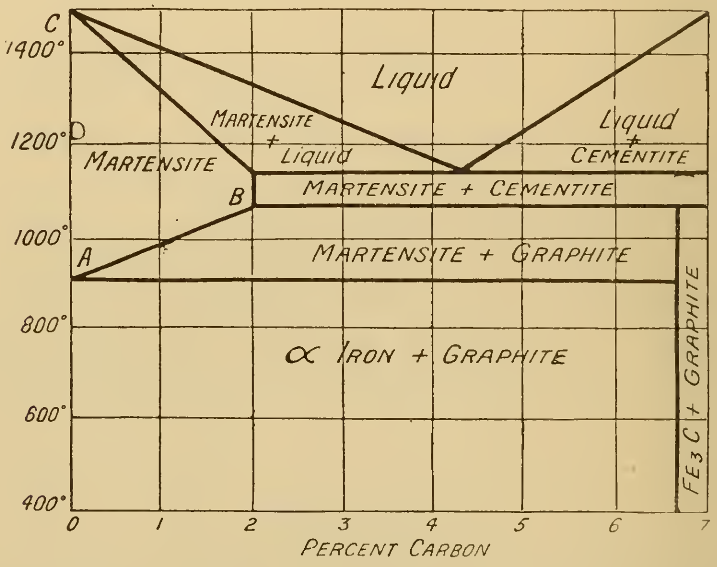

C
1400°
1200°
1000°
800°
600°
400°
D
A
B
Liquid
Martensite + Liquid
Liquid + Cementite
Martensite
Martensite + Cementite
Martensite + Graphite
α Iron + Graphite
Fe₃C + Graphite
0
1
2
3
4
5
6
7
Percent Carbon

Fig. 7.—Diagram for Heating.

The line drawn AB, Fig. 7, from 900° on the pure iron side of the diagram to the point at 1080°, and 2 per cent. of carbon divides the martensitic area from that of martensite and graphite; that is to say, an alloy containing between 0 and 2 per cent. of carbon will have to be heated to a temperature above AB before the graphite will begin to go into solution in the iron; whilst with more than 2 per cent. carbon the temperature required will be above 1080°. This indicates, therefore, that unless the iron be heated above 1080° not more than 2 per cent. of carbon can go into solution.

The diagram for cooling given in Fig. 8 indicates that upon cooling an iron can hold carbon in solution down to a temperature of 700°, at which temperature it is thrown out of solution as carbide, and eventually the latter compound breaks up into iron and graphite. It will be noted that in the construction of the two diagrams Benedicks' theory of allotropy has been taken as being correct, no allowance being made in the diagrams for β iron.

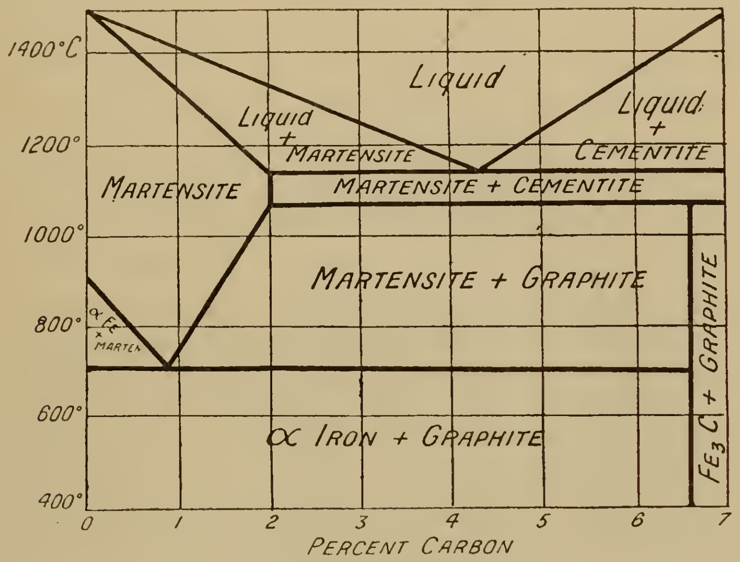


FIG. 8.—Diagram for Cooling.

If what has been suggested is correct, Upton's diagram, Fig. 9, becomes an impossibility. Upton considers that below 700° two carbides can exist, $Fe_3C$ between 600° and 725°, and $Fe_2C$ below 600°. If, however, the stable phase below 700° upon cooling is iron plus graphite such compounds have no existence, and must, at the least, be in a metastable state. Upton's diagram is, however, entirely theoretical and based upon the work of many scientists, and the evidence for the existence of $Fe_2C$ is exceedingly slight. Upton considers that the phases separating from the melt are martensitic plus graphite; that is, in alloys containing more than 2 per cent. of carbon, and that at a temperature of about 1100°, the separated graphite recombines with the iron to form a carbide $Fe_6C$. The present author's photomicrographs, however, clearly shows that carbide of iron, or silico-carbide of iron, separates out of the liquid in the first case, along with the primary austenite. In the alloys employed the silicon reached as high as 9·86 per cent. If, then, with such a large percentage of silicon, carbide separates from the melt, with how much more certainty can it be depended upon that the phases separating from the melt in a pure iron carbon alloy are carbide plus martensite, for the natural tendency is for silicon to decompose the carbide of iron into free iron and graphite. If this does not happen in this case, it certainly will not in an alloy containing no silicon.

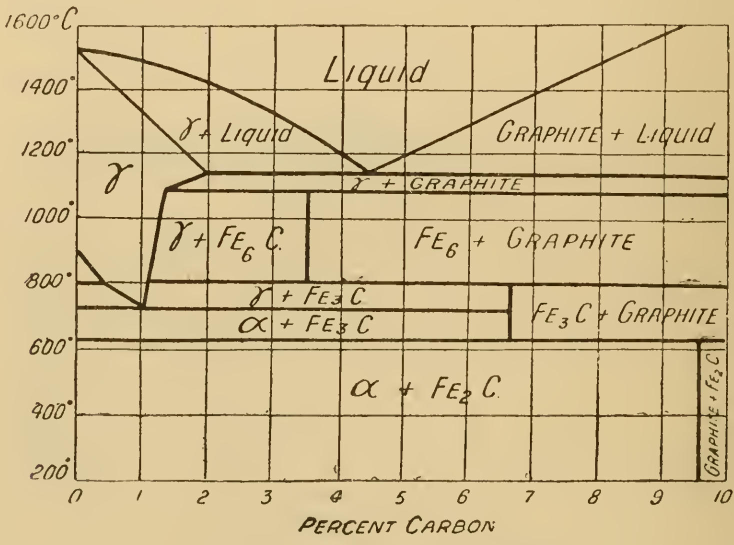


FIG. 9.—Upton's Diagram.

The photomicrographs prove conclusively that carbide separates from the melt, and can exist undecomposed down to a certain temperature not determined, but in all probability about 1100°. Even with silicon as high as 9·86 per cent. this is so. (See Plates I. to IV.)

If the displacing power of silicon for carbon be represented by the factor 0·45, an alloy containing 9·86 per cent. silicon and 2·52 per cent. carbon should be equal in properties to an alloy containing $9 \cdot 86 \times 0 \cdot 45 + 2 \cdot 52 = 6 \cdot 95$ per cent. carbon. It is seen that whilst the Ar3-2 point is very persistent even in high silicon alloys, that 4·5 per cent. silicon is sufficient to eliminate the Ar1 point entirely, and that what Gontermann regarded as the Ar1 change was in reality the Ar3-2, which, according to Gontermann, is rapidly raised by each addition of silicon. It is, indeed, probable that with as much as 10 per cent. silicon it is raised to the temperature of freezing, *α* iron being formed immediately upon freezing, and the carbon thrown out of solution. That silicon also reduces the solubility of carbon, even above 700°, must also be taken into consideration, together with the fact that silicon, when present in a certain amount, is able to effect a decomposition of carbide even when in solution. The fact that 4·5 per cent. silicon will entirely eliminate the Ar1 point necessitates some slight modification of Gontermann's diagram, requiring the addition of a line AB, Fig. 10, running from 4·5 per cent. silicon on the silicon side of the triangle, to the point 6·6 on the iron-carbon side. In this way the diagram is divided into two parts, the area 1 consisting in the normally cooled state of silico-ferrite and cementite, and the area 2 of silico-ferrite plus graphite. Although, as has been stated before, in the absolutely stable state the entire field would consist of silico-ferrite plus graphite, it will be noticed that the usual metastable form of the iron-carbon diagram has here been given in order to conform with Gontermann's diagram.

No. 1 area may further be sub-divided by the line CD into two portions, that to the left being constituted of silico-ferrite plus pearlite, and the part on the right of silico-cementite plus pearlite.

In conclusion, the author wishes to remark that he feels compelled in view of his results to agree with Dr. Stead in considering that the phase first to separate from the melt in a high carbon-silicon alloy is a silico-carbide of iron, both quenching experiments and cooling curves strongly pointing to this. He wishes to thank Mr. W. J. Foster of Darlaston for very kindly providing him with the pig iron used in the research, and he is also much indebted to Professor C. A.

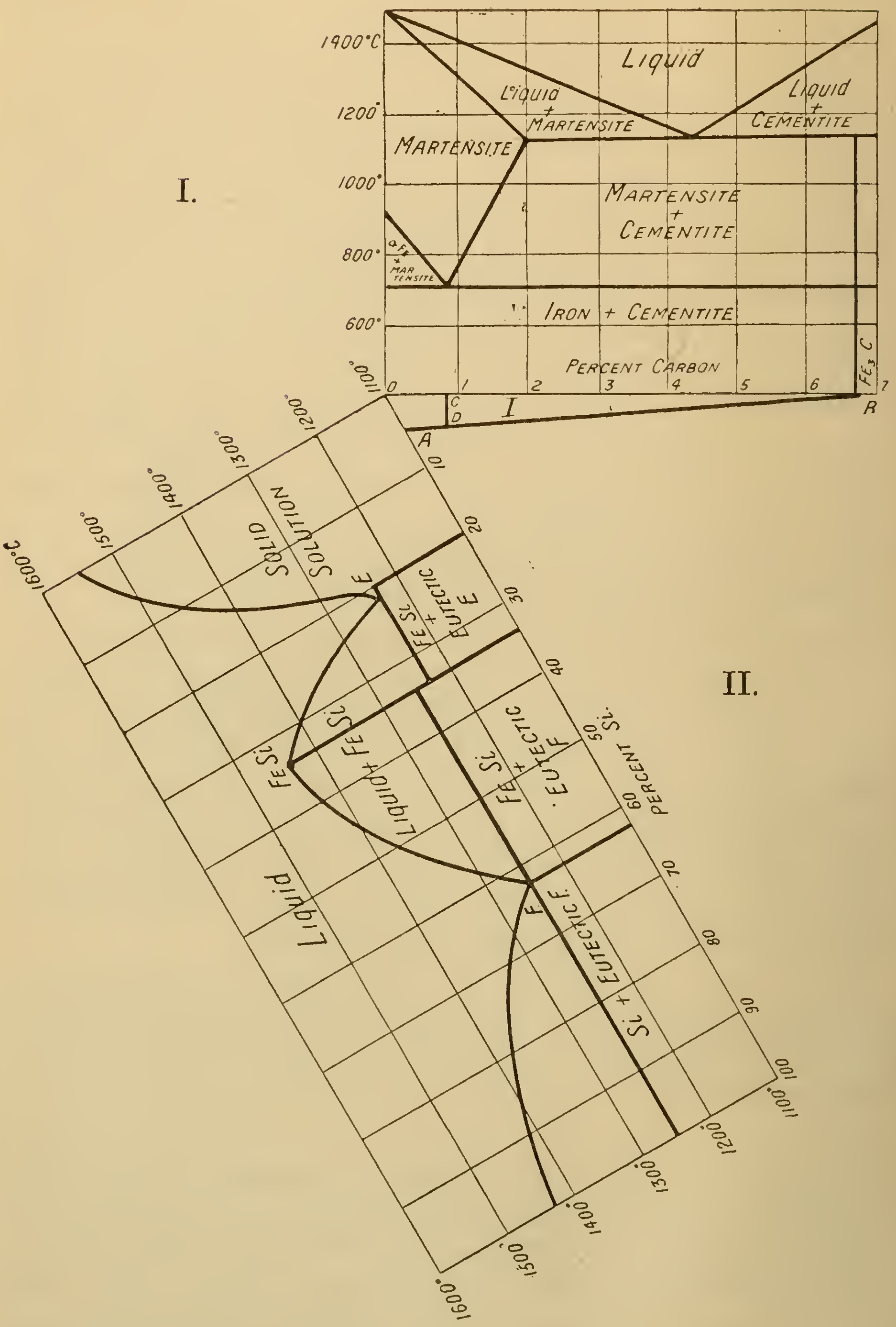
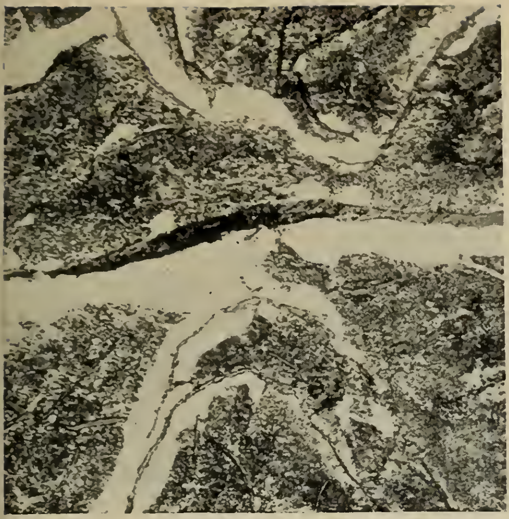
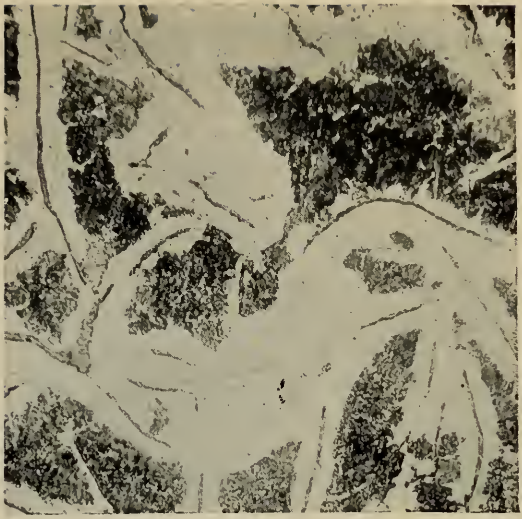

I.
1400°C
1200°
1000°
800°
600°
1100°
Liquid
Liquid + Martensite
Liquid + Cementite
Martensite
Martensite + Cementite
α Fe + Martensite
Iron + Cementite
Percent Carbon
0
1
2
3
4
5
6
7
Fe3 C
C
D
I
A
R
II.
1600°C
1500°
1400°
1300°
1200°
1100°
10
20
30
40
50
60
70
80
90
100
Percent Si.
Solid Solution
E
Fe Si + Eutectic E
Fe Si
Liquid + Fe Si
Fe Si + Eutectic F
F
Liquid
Si + Eutectic F.
1100°
1200°
1300°
1400°
1500°
1600°

FIG. 10.—Gontermann's Diagram modified.



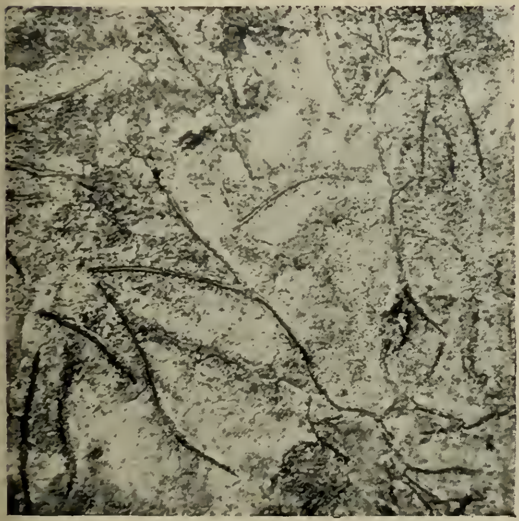
No. 1.

No. 1 pig iron used for most of the experiments. Magnified 200 diameters and reduced to one-half.



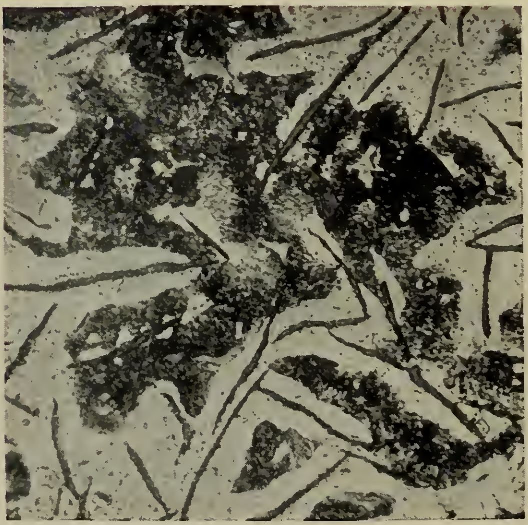
No. 2.

Same iron after remelting and allowing to cool slowly in the furnace. Magnified 200 diameters and reduced to one-half.



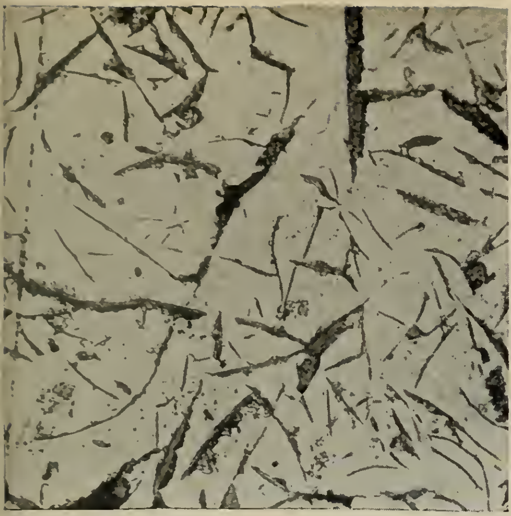
No. 3.

Slowly cooled iron which has been quenched previous to remelting. The pearlite areas are greater in extent than those in No. 2. Magnified 200 diameters and reduced to one-half.



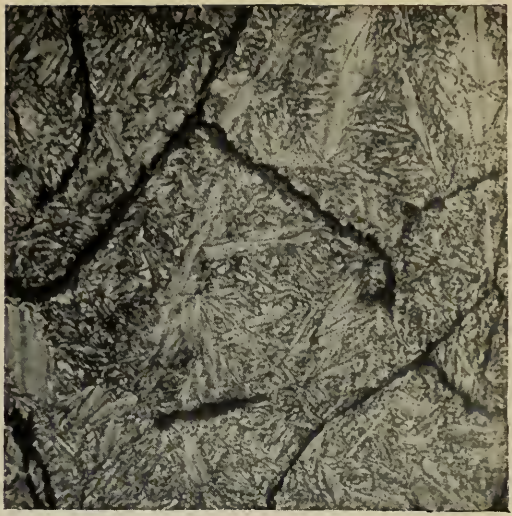
No. 4.

Pearlite area of the 4·18 per cent. silicon iron slowly cooled from the liquid. Probably some of the dark etching part is free carbon resulting from decomposition of the carbide. Magnified 200 diameters and reduced to one-half.



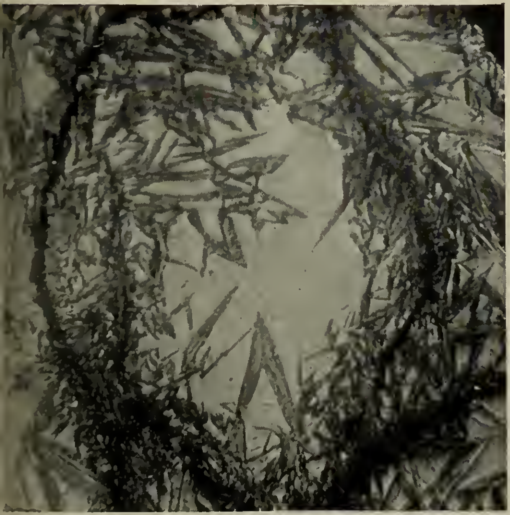
No. 5.

9·86 per cent. silicon alloy after melting and slowly cooling. Entire absence of pearlite, the whole mass being composed of silico-ferrite and free graphite. Magnified 200 diameters and reduced to one-half.



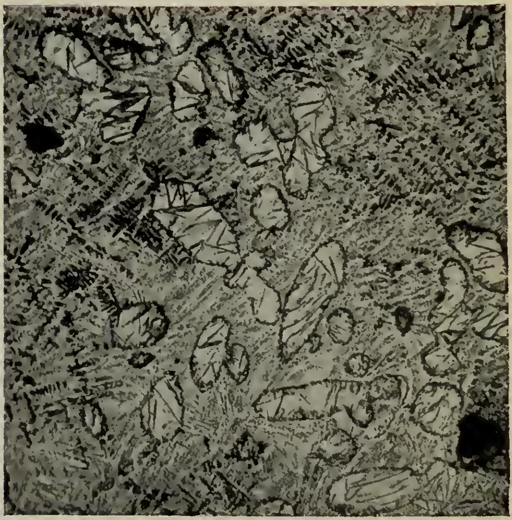
No. 6.

No. 1 pig iron after being heated to 950° for three hours and quenched at that temperature. In the alloy thus heated a decrease in the graphite was noted; the structure, however, is that of homogeneous martensite. Magnified 1000 diameters and reduced to one-half.



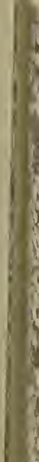
No. 7.

No. 1 pig iron heated to 1120° and quenched from that temperature, showing well-defined austenitic martensitic needles. Note the presence of graphite and the absence of cementite. Magnified 1000 diameters and reduced to one-half.

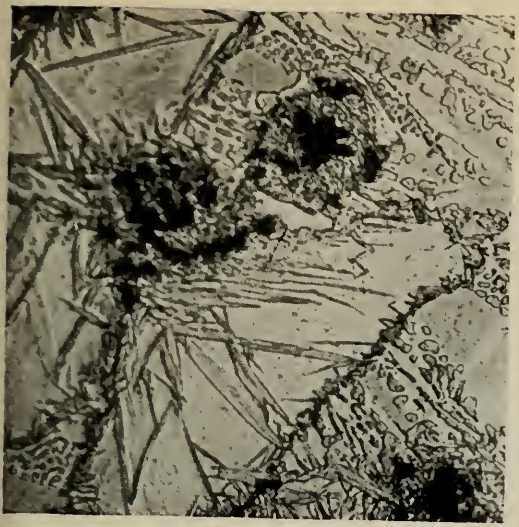


No. 8.

4·18 per cent. silicon alloy quenched from the semi-liquid state, showing austenitic martensitic markings along with the carbide martensite eutectic. Magnified 200 diameters and reduced to one-half.

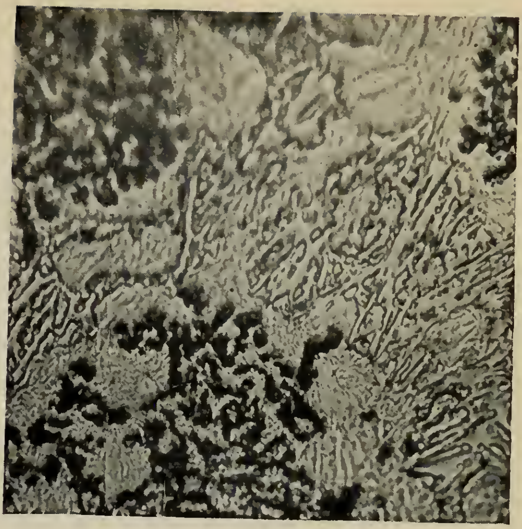


# PLATE III



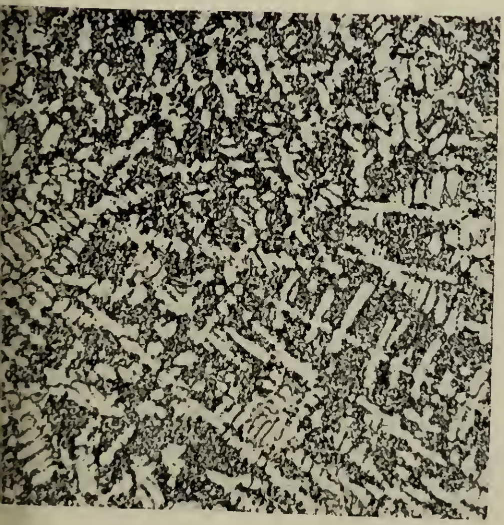
No. 9.

One of the spherical areas shown in No. 8 at higher magnification. The austenitic martensitic markings are surrounded by a ring of graphite, whilst outside this ring are dots and dashes of primary cementite. Magnified 1000 diameters and reduced to one-half.



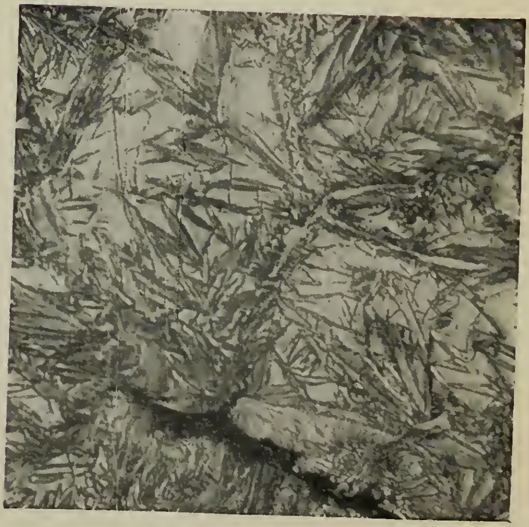
No. 10.

4·18 per cent. silicon alloy, quenched below the freezing temperature, showing the cementite martensite eutectic, and what seems to be freshly deposited carbon appears; probably a decomposition product of the carbide. Magnified 1000 diameters and reduced to one-half.



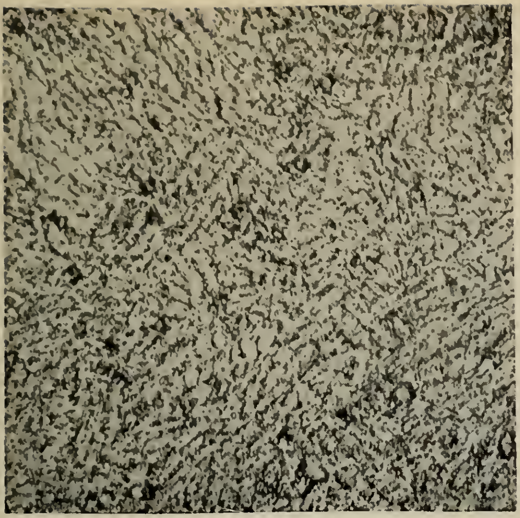
No. 11.

Typical eutectic structure of the 4·18 per cent. silicon alloy quenched from 1120°. Magnified 200 diameters and reduced to one-half.



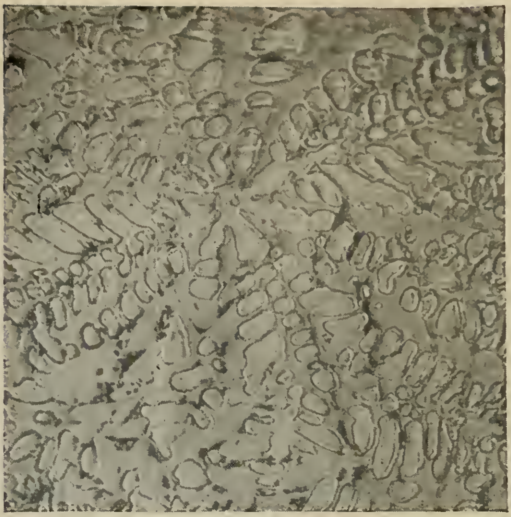
No. 12.

Same as No. 11, more highly magnified, the austenitic martensitic structure being exceedingly clear. Magnified 1000 diameters and reduced to one-half.



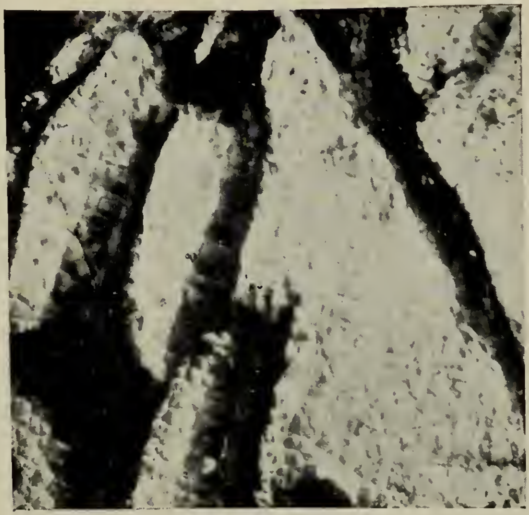
No. 13.

9·86 per cent. alloy quenched from just below the melting point; then allowed to melt and quenched whilst in the plastic condition. Typical eutectic structure. Magnified 200 diameters and reduced to one-half.



No. 14.

Eutectic areas shown in No. 13, showing the carbide in relief in a martensitic matrix. Magnified 1000 diameters and reduced to one-half.



No. 15.

9·86 per cent. silicon alloy heated for some time above 1100° and quenched from that temperature. None of the carbon has gone into solution but remains as before, embedded in a matrix of silico-ferrite. Magnified 1000 diameters and reduced to one-half.

It might be noted that the structure of the 4·18 per cent. silicon alloy was similar to No. 6, when this was heated to, and quenched from, a temperature of 950°.

Edwards for the keen interest which he has shown throughout the investigation, and for the many valuable suggestions he has offered.

This investigation is the outcome of a suggestion offered by Professor H. C. H. Carpenter, to whom the author wishes to express his sincere thanks. The greater part of the work was carried out at the Metallurgical Laboratories, the University of Manchester.

# DETERIORATION OF REFRACTORY MATERIALS.

## WITH SPECIAL REFERENCE TO OPEN-HEARTH PRACTICE.[1]

By H. B. CRONSHAW, B.A., Ph.D., A.R.S.M. (Cambridge).

## INTRODUCTION.

During the last ten years, and especially during the second half of this period, users of the best procurable firebricks have frequently directed attention to the inefficiency of the material supplied to them. This is evidently an outcome of the rapid advances made in metallurgical operations, both as regards output, which means increase in the severity of working conditions, and because of the efforts which are continually being made to economise working expenses. Hence refractory materials have been called upon to cope with more and more exacting requirements, and at the same time it has become clearer to metallurgists that efforts ought to be made to decrease the great expense incurred in the installation and upkeep of furnace linings. Both in America and Great Britain, it has been customary to regard the brick manufacturer as being entirely responsible for this state of affairs. Very probably this is actually true in a great number of cases where the brick manufacturer has failed to keep pace with metallurgical advances and properly to understand the requirements of the consumer. On the other hand, the latter has not, in many cases, been in a position definitely to state these requirements. If the brick manufacturer be not acquainted with the conditions under which his products are to be used, he can hardly be expected to furnish satisfactory materials. An excellent brick may be condemned if

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[1] Report received March 9, 1915.

it happens to be used in the wrong place. The fault is therefore not entirely that of the brick manufacturer, but is shared to some extent by the consumer. Furthermore, there is undoubtedly a lack of proper understanding between the two parties.

The first step towards supplying any particular furnace with a lining, &c., is to ascertain the chief destructive agents at work in every part of it. If these are known, the consumer will understand exactly what kinds of bricks are most suitable for the various parts of his furnaces. It then rests with the brick manufacturer to produce the required material. It appears, however, to be commonly the case that those responsible for the refractory portions of a furnace have prejudices, or else the choice is determined by a costly process of trial and error on a large scale. For instance, some bricks which have been thoroughly burnt are less attractive in appearance than others which have received only partial treatment in this direction. The result is that if the choice is largely determined by the appearance, the manufacturer is hardly encouraged to eliminate one of the most serious sources of trouble, namely, imperfect contraction caused by defective burning. Trial on a large scale is rendered unnecessary if the adverse conditions which prevail in a furnace are fully understood. Further, this does not help the brick manufacturer to abandon the empirical methods which to a large extent still prevail.

It is now generally recognised that such factors as infusibility and chemical composition are not to be taken as the sole indications of the degree of refractoriness of a material, using the term in its broader sense, as indicating the ability to resist all forms of destruction, and not fusion alone. The old idea that a high content of silica was necessarily associated with high refractoriness is also practically dispelled, and it has come to be more clearly recognised that the refractoriness of a given material is not a function of one property alone, but depends on a number of factors which vary in relative importance according to the working conditions which prevail in the place it is used. These conditions, which are of both a physical and chemical nature, vary in the several parts of the same furnace, and in different types of furnaces. They vary in character and in relative importance. A firebrick must therefore have special chemical and physical properties to withstand these influences.

Chemical analyses are, of course, very important, for, besides indicating the extent to which the material will resist destruction of a chemical nature, they supplement observations under the microscope.

At this point it is desirable to draw attention to the possibilities underlying the use of the petrological microscope as an important accessory in determining whether a clay or quartz-rock is suitable for firebricks, and also for observing the changes which occur in a firebrick on burning. The chemical and physical properties of a clay, or any raw material used in brick-making, are determined by its mineralogical composition and texture; and if the latter could be conveniently and accurately estimated, they would no doubt constitute the most scientific basis for a classification. The various processes by which the mineralogical constitution of a clay is ascertained are particularly complex and tedious. On the other hand, practically the same results could be obtained by making use of a high-power microscope. It would, of course, be impossible to adopt the ordinary methods of cutting thin sections in the case of clays in their plastic condition, but if they were burnt hard and soaked in Canada balsam, there ought to be no particular difficulty in obtaining sections thin enough for examination. Possibly similar results would be obtained without burning, supposing the material to be warmed with the balsam and then carefully ground. It must be remembered, however, that some of the constituents of clays are in such a very fine state of subdivision that their detection is a matter of extreme difficulty, whilst in many cases it becomes almost impossible to effect a determination with any degree of confidence. On the other hand, quartzites, sandstones, grits, and other rocks which are used in brick manufacture can easily be cut into thin sections, and conveniently examined under the microscope. In this way a very good idea can be obtained of the amount of free quartz in the material, whether the grains are rounded, angular, or sub-angular, and how they are distributed in the material,—that is, whether they are closely packed together to form a mosaic, or whether they are more or less widely separated from one another by the matrix, which is a consideration of considerable importance. Further, it would be possible to judge the variation in size of the grains, whether they are cracked and free from inclusions, and whether the matrix consists of lime or ferric oxide, or both. Observations of this kind have a direct bearing on the technical value of brick-making materials.

In judging a particular clay as regards its suitability for firebricks, determination of the softening point is a matter of first importance. In this way Mellor has classified clays and shales, first of all, into two main groups,—refractory clays which soften above 1500°, and non-refractory clays softening below this temperature. The latter, which include ball and pottery clays, brick and terra-cotta clays, marls, gault clays, &c., may be left out of consideration for the present purposes. Refractory clays include practically all the so-called fireclays, very few of which soften below 1500° C. They are further divided into :

(1) Low grade fireclays, softening between 1500° and 1650°
(2) Medium ,, ,, ,, 1650° and 1750°
(3) High ,, ,, ,, above 1750°

The determination of softening point is made under certain fixed conditions which, for instance, take into account the rate at which the temperature rises.

A further use for the microscope is found in its application to the examination of firebricks, by both manufacturer and consumer. As in the case of the raw materials, the mineralogical composition can be qualitatively, and to some extent quantitatively determined, especially if supplemented by chemical analyses. Apart from this, it is also possible to see how much internal fusion has taken place in burning, and hence be in a position to form an opinion as to whether the bricks have received adequate treatment in this respect,—an observation which would also lead one to estimate the degree to which additional fluxing would be likely to take place at protracted furnace temperatures. Furthermore, a simple examination would enable the manufacturer to detect the particular stage of burning at which this fluxing is practically complete, a point which roughly coincides with the elimination of residual contraction. The texture of a brick can, of course, be most satisfactorily studied under the microscope. Important features are the minute structures of grog and groundmass, which include frequency, shape, and variation in size of grog particles, together with the quartz fragments which compose them, and the structure, amount, and distribution of matrix in both groundmass and grog.

The questions opened up by the above considerations may be summarised as follows:—

I. What are the causes and effects of destruction of refractory materials installed in the various parts of any particular type of furnace?

II. Is it possible to arrange these factors in order of their relative importance as destructive agents?

III. Having once defined the nature and relative importance of the destructive agents at work in any particular type of furnace, to what extent can one reduce their effects, either
  (*a*) By eliminating the agents themselves, or
  (*b*) By selecting bricks with properties best adapted to withstand the agents in question?

IV. How far can the brick manufacturer produce specified properties in his products?

## OPEN-HEARTH FURNACES.

The open-hearth regenerative furnace for making steel will be considered first, on account of its importance and because of the extraordinary rapid destruction which the lining undergoes. The more modern kinds of open-hearth furnace, and the still more recent Talbot furnace, are the types which appear to find greatest favour at the present time, and these were consequently selected for detailed study.

Apart from the iron and steel structure which constitutes the actual framework or skeleton, open-hearth furnaces are built up of various kinds of the most refractory firebricks at present obtainable. With regard to a single furnace, the refractory materials are required to perform special functions which depend on their particular position in the furnace, and furthermore, they are subjected to various destructive agents of both a physical and chemical nature. It is these conditions which determine the various qualities and kinds of firebricks used in building up the body, blocks, and regenerators of any particular open-hearth furnace. Speaking in a general way, the arrangement of the refractory materials is very similar for all these furnaces. As regards the body-lining, however, one important difference does exist which is conveniently used as a means of dividing the furnaces into two classes. This is dependent on the difference in chemical conditions determined by the particular process adopted for making steel,—that is, whether acid or basic.

In the case of furnaces working on the acid process, the roof, sides, and blocks are constructed of silica bricks, whilst the hearth is made up of a number of layers of fritted sand, resting on a stepped arrangement of silica bricks which constitutes the bottom of the furnace. The sand is banked up to the level of the doors. An inferior type of brick is often used for part of the blocks. The roof of an actual example was 9 inches in thickness, the sides 18 inches, whilst the bottom consisted of 6 inches of silica bricks and 15 inches of fritted sand. It was continuously worked from mid-day on Sunday till mid-day on Saturday, with Saturday afternoon left for the repairs of a more or less serious character which a lining always requires. The work is done under very trying conditions, and as quickly as possible. Firing was resumed at perhaps three o'clock on Sunday morning, and at about seven o'clock the furnace received its first charge of cold pig iron. Subsequent charges may have consisted, for example, of pig iron, scrap, and ferric oxide in various forms. Furnaces of this type, without slag-pockets, usually run about sixteen weeks, or 144 heats, before being stopped for serious repairs or partial rebuilding, which may consist in the erection of a new roof and sides. If, however, slag-pockets are attached, which is always the case in modern furnaces, the length of life is increased to twenty-two weeks, or about 198 heats. In more favourable instances, however, the roof may last double this time if skilfully repaired. The bottom lasts several years before it requires rebuilding. Apparently better results are obtained in America, for, according to Stoughton, an acid furnace will survive as many as 1000 heats. As regards furnaces working on the basic process, quite a large number now in use are built with a roof of silica bricks, the sides partly of silica and partly of magnesia bricks, whilst the bottom consists of magnesia bricks covered with a considerable thickness of magnesian limestone or dolomite. The following is a description of the arrangement for the refractory portions of a modern 150-ton Talbot furnace. The bottom, ends, and a portion of the blocks containing the gas ports are built of magnesia bricks. The same are also used for the back wall to within four courses of the roof, and for the front wall up to the springing of the arches. A mixture of dolomite and tar is rammed on the bottom, and banked up level with the doors. The rest of the furnace—that is, the roof, and parts of the walls—is constructed of silica bricks. The doors are faced with ganister bricks on the inside, and firebricks on the outside. A series of water-cooled pipes pass round the doors, and other sets protect the ports. The joints between the blocks and body of the furnace are made by water-cooled chills. The thickness of the magnesia bottom is 2 feet; that of the dolomite hearth, 12 inches. The sides are 2 feet in width, whilst the roof measures some 18 inches at the centre and 12 inches near the ends. At the end of every heat, repairs are carried out by means of chromite mortar. The brickwork in the neighbourhood of the doors usually calls for a good deal of attention in this respect. At the end of every week—that is, on Saturday afternoon—the gas is cut off, the blocks drawn back, and all faulty places repaired. Ganister mortar is freely used in the blocks. Near the water-pipes chromite is employed, whilst crushed dolomite is thrown on to the bottom of the furnace. After about eighteen weeks the front wall and roof usually require rebuilding. In certain places, the latter is often found reduced to a thickness of some

2 or 3 inches. On the other hand, the back wall, which for the most part consists of magnesia, seldom requires taking down and entirely rebuilding. At the end of the usual eighteen weeks' run, it generally varies from about 9 inches in thickness at the upper parts to about 18 inches, where it meets the dolomite hearth. The bottom lasts several years. Another example may be taken to illustrate the Siemens type of furnace. Magnesia bricks are used in the bottom, and crushed dolomite for the hearth. The sides are built of a somewhat different quality of the same for three courses above the fore-hearth plate. The roof, blocks, and upper portions of the sides consist of silica bricks, whilst the lower parts of the blocks are built of an inferior silica brick. In the course of about fifteen weeks the roof, which was originally 12 inches in thickness, is worn down to about 4 inches. The bottoms are said to have a lifetime of from seven to nine years. On the authority of F. T. Havard, it would be considered very satisfactory in American practice if a furnace survived 350 heats, corresponding to from eighteen to twenty-four weeks.

Other arrangements of refractory materials in basic furnaces are to some extent still adopted. The roof, walls, and bottom may be built of silica bricks, whilst the hearth consists of the usual basic material. Another arrangement consists in constructing the entire bottom, and a portion of the sides, of basic material, and the rest of the sides, together with the roof, of silica bricks. Chromite is often inserted in the walls at the junction between basic and acid materials.

Several methods have been used for detailed construction of the hearth. At one time the hearth was built up entirely of basic bricks. This, however, was not a success. Another method consisted in first ramming the bottom with crushed dolomite and tar, and then drying the whole gradually prior to subjecting it to higher temperatures. In this case also the results were not satisfactory. The best results are apparently obtained when the basic material is fritted on in layers in a way similar to that employed in acid furnaces. The bottom itself may consist of silica and magnesia bricks. The latter give the best results, but are more expensive. According to Harbord, the hearths in some of the American furnaces are built up first with a course of firebricks, followed by magnesia bricks, and then the usual layers of fritted basic material.

The arrangement of bricks in the blocks and regenerators is very much the same for both acid and basic furnaces. Various forms of blocks appear to have been tried, but the present tendency seems to be towards a reduction in size. Very often somewhat inferior bricks are used for certain parts, but it is questionable whether any advantage is gained by doing so. On the other hand, in the case of modern Talbot furnaces, the more expensive magnesia bricks are built into the gas ports. As regards the regenerators, ganister bricks appear to find general use for the checkerwork. The lifetime usually assigned to regenerators attached to large Talbot furnaces is about eighteen months for the gas chambers, and twelve months in the case of the air chambers. At the end of this time the checkerwork has to be rebuilt.

It is thus evident that the question of refractories is a very important one for the steelmaker. The initial cost of the immense number of bricks used in building up the various parts is very considerable. In addition to this, the material represents a continuous source of heavy expense. The bricks are continually being repaired and replaced, which involves labour employed under adverse conditions and considerable loss of time. Materials and labour are both expensive. The case is particularly serious for basic furnaces, where the rate of destruction in the body is more rapid than with acid furnaces. The checkerwork of the regenerators also suffers very considerably, and as a result their efficiency is very quickly impaired. This leads to loss of time, as more time is needed for completing a heat, and possibly to cold heats. Therefore every effort ought to be made to reduce the rate of destruction to a mimimum, and any device, even though it may only partially contribute towards this end, is an important matter.

The destructive effects which have so far been discussed in a very general way are to be traced to a variety of agencies, which mutually assist one another in their work. This can easily be realised by examining the interior of an abandoned furnace. The surface of the roof has been worn away in quite an irregular manner, leaving hollows and grooves. The sides and walls are glazed, and the bricks are darkened in colour. The latter have apparently undergone considerable changes in texture, and to some extent in composition. Furthermore, portions of the refractory lining have cracked, or even broken away. In making a more detailed investigation into these agencies, it is, however, convenient to consider each separately. Broadly speaking, they can be divided into two classes, physical and chemical. To the former belong such factors as abrasion, volume changes; and to the latter, changes due to temperature alone, and slagging effects. In the following an attempt will be made to estimate the relative importance of these in every part of the furnace.

## Body of Furnace.

*Abrasion.*—Examination of the interior of the body of a furnace after, say fourteen to eighteen weeks, shows that erosion of the roof has taken place, not uniformly over the whole surface, but somewhat irregularly, so as to leave furrows, hollows, and crevices. The most pronounced effects occur in the central portions, usually including an area about 6 feet square situated above the middle door. At either end well-marked furrows spread out fanwise from the air port. Another example of localised destruction is to be found in the peculiar form assumed by the roof of a Siemens furnace, having its two air ports situated at the upper corners. Here denudation proceeds most rapidly along either side of the roof, so as to form two long hollows separated by a broad ridge. These peculiarities can be best ascribed to the abrasive action of fine dust swept through the furnace by the producer-gas. The destructive effect of solid particles impelled either by wind or forced draught is widely recognised. Familiar instances are the sand-blast, and the wind erosion in dry regions. The general effect of these agencies is to round off projections, and produce uniform, polished surfaces. In surfaces of unequal hardness the softer parts are selected for more rapid erosion. A continuous bombardment of the roof by innumerable particles of flue-dust must constitute an effective means of destruction. It is, however, very probable that actual erosion only takes place at the incoming end of the furnace, and that the central portions practically escape. This results from two causes. The velocity with which the dust particles are carried along by the gases will diminish when once they approach the middle of the furnace, and therefore a corresponding diminution in their force of impact will also take place. Secondly, most of the particles will become fused when they get well within the furnace, and consequently will simply stick to the roof and sides, and, instead of diminishing, will actually add to their thickness. It is quite possible, however, that direct contact between portions of the flame and the roof might also, in some measure, account for these grooves and surface undulations. The disastrous effects due to the "cutting action" of the flame make themselves plainly evident in the rapid destruction of the ports.

*Volume Changes.*—When a firebrick, or body of firebrick, is subjected to temperature variations, it generally undergoes a corresponding change in volume. These temperature fluctuations arise from a number of causes,—when the lining receives its first heat, for example, or when the gas is cut off for the usual week-end repairs. Rapid changes in temperature of a more or less local character also occur when the doors are opened, and cold material charged into the furnace. These temperature variations have a two-fold effect. In the first place, the lining suffers as a whole. The roof, walls, hearth, and other parts of the furnace expand on heating. Also, in most cases owing to a permanent expansion and contraction slowly taking place after the temperature has attained a maximum, the brickwork does not reoccupy its original volume when the furnace cools down to normal temperature again. Besides this, differential movements set in when the temperature is raised or lowered. Thus it is obvious that unless proper precautions are taken, the lining would be very soon destroyed from these causes alone. There are numerous cases on record where neglect to apply these precautions has resulted in the rapid collapse of the lining. The second result of temperature variation is the production of strains and differential movements within the bricks themselves. The tendency is thus towards the production of cracks and general disintegration. Fragments of bricks may drop from the roof and sides, and cracks of a more or less serious character may be produced, offering access to fluxing agents, such as vapours, fine particles of dust, and molten slag, or, in the case of the hearth, of molten metal, which exerts a very effective disruptive force.

*Heat and Fluxes.*—These act conjointly; the independent efforts of either would, relatively speaking, produce slight results. Most furnaces are equipped with linings made from materials which soften at temperatures higher than `those attained during working conditions, that is, providing the material is not directly exposed to the full play of the flame. How important the latter consideration may become is shown by the rapid erosion of roofs in the earlier forms of Siemens' furnace. They were built with a depression in the middle, and thus came under the direct influence of the flame. There appears to be no really reliable information concerning the temperatures holding in different parts of the furnace. Le Chatelier estimates the temperature of gas entering the body from the regenerators as 1200° C., and the air as 1000° C. As a result of a large number of observations made on the gas passing from the regenerators into the body of a 150-ton Talbot furnace, the temperature may be regarded as varying between 1000° and 1200° C. The temperature of the flame must therefore rise considerably above this, and hence the importance of preventing the flame from impinging on the brickwork. It would be interesting to make direct measurements of the temperatures attained by the inner surface of roof and walls, particularly the roof. Experienced chemists estimate it as being something like 1500° C. If so, this is rather dangerously near the softening point of silica bricks. Kanolt gives 1700° to 1750° C. as the softening point of silica bricks, the determination having been made on three samples. A magnesia brick, on the other hand, is recorded as softening at 2165° C. Simple examination of bricks taken from the roofs of abandoned furnaces is not sufficient to determine whether the temperature alone was high enough to fuse the exposed faces, because the effects are completely masked by the interference of fluxes. It is, however, clear that the bricks do not soften to any appreciable extent, as they preserve their form in spite of being under considerable pressure. Microscopic examination, however, makes it clear that the surface of the roof is exposed to temperatures well under the melting point of quartz. Certain changes do take place which are the outcome of protracted exposure to high temperature alone. In the case of silica bricks such changes for the most part constitute processes of partial vitrification, recrystallisation, and polymorphism. As regards the latter, Fenner, in 1913, made an exhaustive inquiry into the stability relations of quartz. Speaking very briefly, he showed that at approximately 870° C. quartz inverts into $\beta$-tridymite, at 1470° C. this changes to $\beta$-cristobalite, and at 1625° C. the latter passes into the amorphous variety of quartz or silica-glass. As might be expected, similar changes are found to have actually taken place in furnace bricks. It is important to point out here that, as far as the roof bricks are concerned, practically no slag seems to have penetrated into the interior. The fluxing processes are confined to the surface. This is probably due to the fact that the fused material will be swept away as soon as it is formed. Fig. 1, Plate V., is a photograph of a high class silica brick taken from the central portion of the roof of a 150-ton Talbot furnace after a period of eighteen weeks. Its original length was 12 inches, which has been reduced in reproduction. For convenience of description, it has been divided into four portions—A, B, C, and D. The portion A is next to the exposed surface of the brick, and consists of a light grey band about 1 inch in width. The outer surface is fused, but the thickness of slag is very small, and sharply marked off from the interior. Next to this comes the portion B, about 2 inches in width, which is similar in texture to A, but differs remarkably in colour, being practically black, relieved by a few pieces of white grog. This grades more or less sharply into the section C, which is dark olive green in colour, and crowded with angular pieces of grog. Lastly, there is a narrow strip of comparatively unaltered material. Sections taken from these various parts and examined under the microscope revealed a series of very interesting changes. A section, cut from an unused brick of the same kind, shows angular fragments of grog embedded in a dark-brown groundmass. The grog, when examined under a high power, is found to be made up of small sub-angular fragments of quartz closely packed together, and enclosing numbers of minute inclusions and bubbles. They are fairly uniform in size, and are separated from one another by what appears to be oxide of iron. On the other hand, the groundmass consists of larger fragments of quartz, which vary considerably in size, embedded in a brownish matrix of, apparently, oxide of iron and lime. In the partly altered portion D, at the lower end of the brick, the grog has not undergone any noticeable alteration. The groundmass, however, is completely changed. The irregular fragments of quartz have disappeared, and in their place are minute well-shaped quartz crystals embedded in brownish glass, which probably also contains a certain amount of undissolved iron oxide. Examination of Section C shows that the grog is still unaltered, whilst in the groundmass the quartz crystals have become somewhat larger, clearer, and more sharply outlined. In B the particles of grog have undergone recrystallisation in quite a remarkable manner, so that they now consist of extremely minute quartz crystals embedded in a brown, glassy matrix. The quartz of the groundmass has grown considerably into clear, well-formed crystals, which show evidences of being in a strained condition. Further, the glassy matrix has developed quite a number of extremely small skeleton crystals. In the last and most advanced phase, represented by the light-coloured band A, a further change has resulted in the quartz crystals becoming converted into a mass of overlapping and partly idiomorphic scales, with a very low birefringence. These are evidently crystals of tridymite. In spite of this change, the original quartz crystals have retained their shape, the tridymite having completely replaced them. This applies to both grog and groundmass.

It is a well-known fact that, in conjunction with temperature, fluxes play an extremely important part in the process of denudation. They vary in nature and origin. The violent spurting of the bath of slag at certain stages in the process constitutes one possible source. Another is the dust which is brought in by the producer-gas. Furthermore, a considerable amount of fluxing material in a fine state of division is introduced during charging, and some of this must be hurled against the roof by the inrush of air through the open doors. The particles carried along by the producer-gas must be raised to a high temperature during their passage through the regenerators, but when they are well within the body of the furnace a certain proportion very probably fuses. Some of this sticks to the roof and sides, whilst the rest is carried through the block into the regenerators. In any case, the internal surface of the furnace is in a fused or partly fused condition, and thus acts as a very efficient dust-catcher. The fluxing process is therefore rapidly promoted, and, as the fused material is swept away, fresh surfaces are exposed for attack. Evidently the rate of denudation is somewhat accelerated by the presence of cracks and by increasing the porosity of the material, although the latter consideration is not so serious a matter as might at first be supposed, on account of the inability of the slag to penetrate into the interior. In this case the importance of fluxing as a denuding process is to a large extent dependent on the constant removal of the slag and the addition of fresh supplies of fluxes to surfaces, which are maintained newly exposed by this removal of waste products. An analysis of the fused portion showed an addition of lime and oxide of iron. The former is evidently derived from the charges, and the latter partly from this source and partly from the producer dust.

*Workmanship.*—Under this heading, attention is directed towards the importance of seeing that the bricks in every part of the lining are set close together, with the object of making the joints as narrow as possible. In certain places this is not possible, because room for expansion of the masonry must be allowed for. It is clear that the joints will form lines of greatest weakness, so that the narrower they are the better. The roof of an abandoned furnace clearly shows that this is actually the case. In the walls, and in many places in the roof, shallow fissures mark the joints, and the surfaces have a kind of embossed appearance. Actual observation leads one to the opinion that far too much mortar is used. To a large extent this is due not so much to defective workmanship, as to the

PLATE V

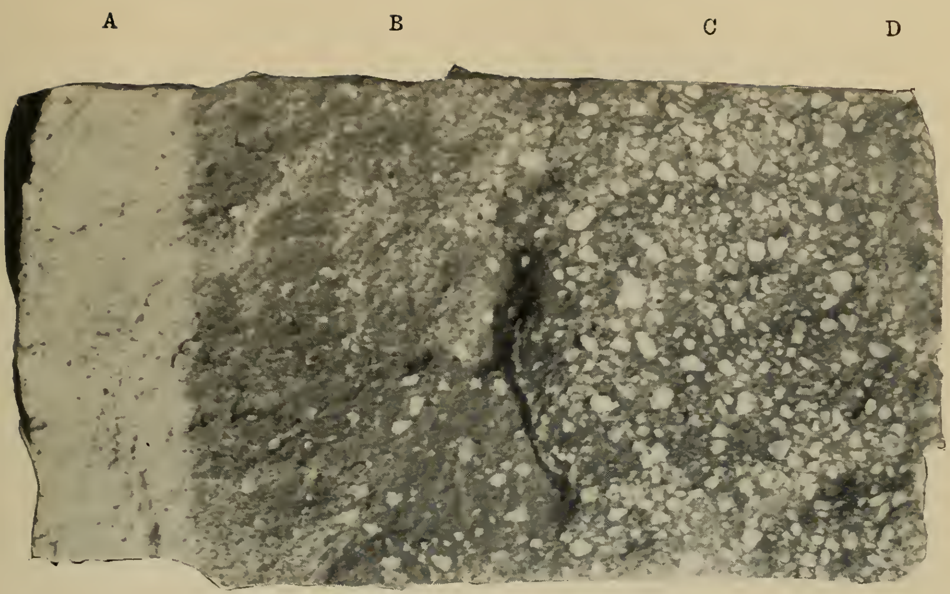

FIG. 1.—Silica Brick. Reduced to about one-third natural size.

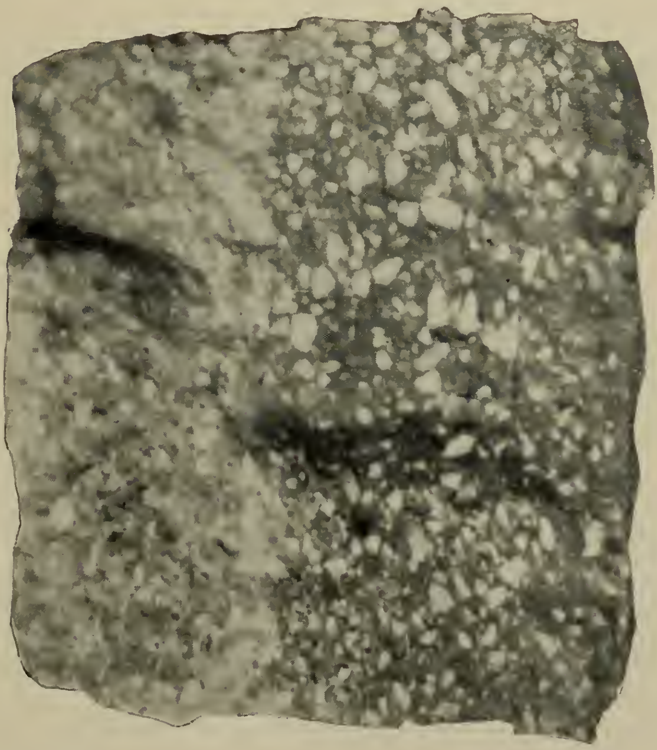

FIG. 2.—Brick from Air Flue of Talbot Furnace.

fact that even the best bricks show remarkable variations in size and form. In very many instances the faces are rounded, whilst in most cases there is a more or less serious divergence from standard sizes. Below is given a series of measurements made on silica bricks used in the roof. They were chosen at random.

8·7×4·7×2·9 inches.
8·9×4·6×2·9 ,,
8·8×4·5×2·8 ,,
9·0×4·6×2·9 ,,
8·8×4·7×3·0 ,,
8·8×4·6×2·9 ,,
8·9×4·6×3·0 ,,
8·8×4·6×2·8 ,,
8·8×4·8×3·0 ,,
8·8×4·7×2·8 ,,

8·8×4·6×2·9 inches.
8·8×4·6×2·9 ,,
9·0×4·5×2·9 ,,
8·9×4·6×2·9 ,,
8·9×4·7×2·9 ,,
8·8×4·7×2·8 ,,
8·9×4·6×2·9 ,,
8·9×4·7×2·9 ,,
9·0×4·6×2·9 ,,
9·0×4·6×2·9 ,,

Similar variations were found in magnesia, ganister, and other bricks.

## PORT-BLOCKS.

The brickwork in the port-blocks suffers under influences which are similar to those obtaining in the body of the furnace, though somewhat modified. Denudation is particularly intense at the ports, and is by no means eliminated by use of water-cooled tubes. In other parts the temperature is not so high, probably in the neighbourhood of 1100° C.; although, on the other hand, the action of the dust must be rendered more intense on account of its being confined in less space. In any case, the surface of the bricks is fluxed, as can easily be seen by looking into the flues soon after the gas is cut off and the blocks drawn back. Fig. 2, Plate V., for example, shows a portion of a brick taken from the air flue of a large Talbot furnace. A section taken at the fused surface showed, when examined under the microscope, well-formed crystals of secondary quartz embedded in a yellowish glass. The pieces of grog had been converted into an isotropic glass, which was somewhat clouded owing to the presence of fine inclusions. Another section, taken from a silica brick which had been built into the block of a Siemens basic furnace, showed the same general features, with the exception that the glass in the groundmass was crowded with skeleton crystals of magnetite.

## Regenerators.

The chief troubles in the regenerators are undoubtedly due to the slagging effects of dust. The results of this are particularly serious and well marked. Undesirable effects begin to appear very soon after the checkers have been built up. For instance, the regenerators attached to a 150-ton Talbot furnace had to be opened for inspection and general cleaning only 14½ weeks after the checkerwork had been erected. On this occasion the upper surfaces of the bricks were thickly covered with a chocolate-brown dust, which had fused at its contact with the bricks. This gave rise to a dark-coloured, viscous slag, which had run over the sides of the bricks, and collected into stalactites on their under surfaces. Thus when the regenerators are in use this slag must drip through the checkerwork from brick to brick. Generally speaking, the bricks themselves had retained their form, and were not noticeably reduced in size. A certain number were fractured, and had to be removed, but the majority seemed to be fairly sound. In the air-chambers there appeared to be more slag, and the evidences of destruction were more noticeable. The internal structure of the bricks had not undergone any marked change. The central portions were yellowish in colour whilst the outer portions were bleached, and to some extent fused, but textural changes had not progressed very far into the interior. Within the gas-chamber the same general features obtained. There appeared to be quite as much dust, but fusion, and consequent slag formation, had gone on to a considerably less extent. The colour of fractured surfaces was also different, being grey instead of yellow. In the case of a set of regenerators attached to a small basic Siemens furnace provided with slag-pockets, the fluxing process had proceeded to a very advanced stage. The bricks in the air-chamber had been in use for about a year, whilst in the gas-chamber they had run for a period of two years. Most of them were very considerably reduced in size. The upper surfaces were somewhat depressed in the middle, with numerous holes reaching into the interior. In many instances the whole of the bricks had been reduced to a partly fused and stonelike condition. Thus, unlike the state of affairs which exists in the case of the roof bricks, the slag which collects in the hollowed surfaces of these checker bricks is allowed gradually to work its way into their interior. This, of course, is particularly the case if the bricks happen to possess a marked degree of porosity, or if they happen to develop internal cracks at all readily.

As regards the length of time which these regenerators usually run before they are opened, and the checkerwork rebuilt, the gas-chambers in a large steelworks where Talbot furnaces were being used were allowed to run for eighteen months, and the air-chambers for twelve months, before being completely rebuilt. In another instance, where basic Siemens furnaces were in use, the gas- and air-chambers survived twenty-four and twelve months respectively, whilst for a particular set of acid Siemens furnaces, both pairs of chambers were only allowed to run for forty weeks. In all these examples slag-pockets were provided, and ganister bricks were used in the checkers. Slag-pockets appear to have a considerable effect on the life of regenerators. This can easily be understood when one considers that the slag which accumulates at the bottom of a pocket, attached to (say) a small basic Siemens furnace, very often collects at the rate of about a foot in depth per month.

So much for a general consideration of the destructive effects. The following set of analyses throws additional light on the details involved in the process.

| | *A* | *B* | *C* | *D* | *E* |
|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| $SiO_2$ . . . . | 59·80 | 86·34 | 83·62 | 12·70 | 30·5 |
| $Al_2O_3$ . . . . | 5·50 | 7·98 | 10·97 | 60·70 | 15·8 |
| $Fe_2O_3$ . . . . | 20·57 | | | | 28·2 |
| CaO . . . . | 11·90 | 2·68 | 4·73 | 26·30 | 4·1 |
| MgO . . . . | ... | Trace | Trace | 2·19 | 0·6 |
| Ignition loss . . | ... | 0·16 | 0·16 | ... | 10·2 |
| | | | ... | ... | $K_2O$ 1·9 |
| | | | ... | ... | $Na_2O$ 1·2 |
| | | | ... | ... | $SO_3$ 5·8 |
| | | | ... | ... | $TiO_2$ 1·1 |
| | | | 99·48 | 101·99 | 99·4 |

*A.*—Partial analysis of slag taken from the slag-pocket of the furnace mentioned under B and C.

*B.*—Partial analysis of the interior of a checker brick taken, after two years' use, from the gas-chamber of a small basic Siemens furnace.

*C.*—Analysis of the surface portions of the same brick.

*D.*—Analysis of checker dust taken after 14½ weeks from the gas-chamber of a large Talbot furnace.

*E.*—Analysis of producer fuel ash given by Dr. Mellor.

A consideration of analysis D makes it clear that the dust which collects amongst the checkerwork is very rich in ferric oxide and lime, and also contains a surprisingly large amount of magnesia. Comparing this with the analysis given by Dr. Mellor, it becomes evident that a large portion of the oxide of iron, and practically all the lime, must come from the materials charged into the furnace. The small amount of magnesia may be assumed to have its origin in the magnesian limestone, or dolomite, which is thrown into the furnaces whilst repairs to the hearth are being carried out. It seems rather difficult to associate it with the magnesia bricks used for building the furnace walls, although it appears possible that one of the effects of abrasion would be to carry some material forward into the checkers. In any case the magnesia, whatever its origin, materially assists the fluxing action of the iron and lime.

The slag (see analysis A) is remarkable for its relatively high content of silica. From this and other considerations it seems reasonable to infer that, for the most part, it represents drops of slag from the roof, particles of slag which are shot up during the periods of violent ebullition which occasionally occur in the slag bath, small pieces of brick which fall from the roof, and the products of fluxing which goes on in the block and slag-chamber itself. Further, it is very probable that the slag-pocket serves to retain only a very small fraction of the dust. It collects the drops of slag and coarse particles, together with pieces of brick, which would otherwise produce disastrous results amongst the checkerwork, but it cannot be regarded as an efficient dust destroyer.

To supplement the analyses, a few sections of fused checker bricks were prepared for microscopic examination. One, for example, was taken at the surface of a brick which had been exposed for a year in the air-chamber, and another, corresponding to analysis B, was taken from the interior of a similar brick, after two years' use in the gas-chamber. Both showed a brown glassy groundmass containing clusters of minute secondary crystals. In the former there were still patches of unaltered quartz fragments, which corresponded to the white pieces of grog which showed up very clearly in hand specimens. In the second case, however, there was no quartz to be seen, and the secondary crystals were larger, but less plentiful.

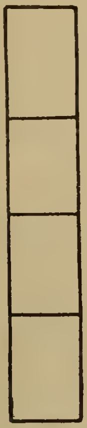

FIG. 3.

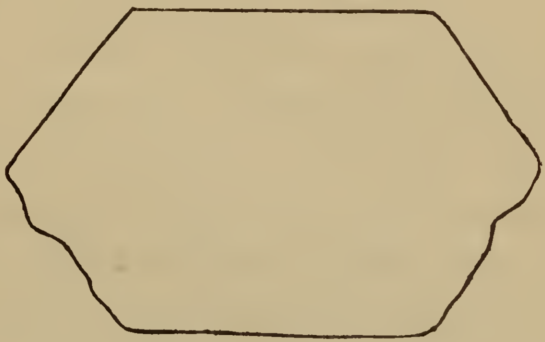

FIG. 4.

In both cases the groundmass was glassy and isotropic, and in certain places nearly black in colour. The secondary crystals, however, formed an interesting feature. They are extremely small, colourless, and lath-shaped (see Fig. 3), and for the most part without terminal faces. They are often fractured transversely, and show straight extinction, and have a low birefringence. Transverse sections are quite frequent, but are too small to permit accurate interfacial measurements being made. Fig. 4 gives a general idea of their form. In many instances zonary growth could be detected. The crystals are too minute for precise determination, although their appearance seems to suggest sillimanite. The low birefringence, however, makes this somewhat doubtful.

## CONCLUSIONS.

So far, the principal causes of destruction in the various parts of open-hearth furnaces have been enumerated, and the effects they produce have been discussed. The next point to discover is, whether it is possible to arrange these destructive agents in order of their relative importance for each section of the furnace.

Taking the body first, and, in particular, the most vulnerable part of it, namely the roof, practically all the erosion which occurs can be attributed to the effects of abrasion, volume changes, and the conjoint influence of heat and fluxes. Assuming that the flame is not allowed to impinge directly on the roof, and that the masonry has been well carried out with bricks of uniform size, there seems no reason to doubt that the combined action of heat and fluxes takes by far the greatest share in the process of wear and tear, which is therefore, for the most part, of a chemical nature. The principal source of trouble is the dust, which is derived partly from the producers, and partly from the charges. It consists chiefly of oxide of iron and lime, and consequently the roof, being built up of quartzose material, is readily attacked, and is eaten away far more rapidly than the basic walls. As pointed out above, the degree of porosity does not influence the rate at which fluxing proceeds as much as it would otherwise do, supposing the slag were allowed to accumulate on the surface of the bricks. As soon as the slag has reached a condition of suitable fluidity, the strong draught through the furnace sweeps it away, and at the same time exposes fresh surfaces for attack by the constantly replenished supplies of fluxing material.

The influence of volume changes probably comes next in relative importance. Large cracks and general disintegration of the lining can, to some extent, be obviated by proper attention to the tie-rods, as well as a careful regulation of the rate at which the furnace is heated or cooled, particularly for the first heat. The small cracks which develop within the bricks themselves prove, in most cases, a source of considerable danger by accelerating the fluxing processes. The trouble is, however, not so serious in the case of the roof, as the slag cannot collect in sufficient quantity to penetrate the cracks. Indeed, the exposed surfaces are remarkable for their smoothness, and freedom from holes and crevices.

The extent to which abrasive action contributes towards the general destruction is rather difficult to estimate, but when considered along with the more obvious influence of heat and fluxes, its importance cannot be said to be very great. This is made additionally clear by the fact that erosion proceeds most rapidly in the central portions of the roof where the influence of abrasion is least felt.

The natural way out of these difficulties is therefore to be found either in suppressing the dust or using a chemically inactive material for the roof, which would, in this case, have to be basic in character. Furthermore, the bricks should have as small a porosity as is possible to obtain without increasing their susceptibility to temperature changes. This also applies to the upper part of the side walls, and to both acid and basic furnaces.

The important part played by the fluxing action of dust has been pointed out in the discussion on regenerators. Here again the trouble is chiefly of a chemical nature. Abrasive action can come into play in only a very limited sense; whilst, on the other hand, the degree of porosity of the checker bricks, and their ability to withstand changes of temperature, become features of considerable importance. In considering the possible ways which might be adopted to insure even a partial elimination of these effects, several methods suggest themselves, all of which must involve considerable practical difficulties, which, however, do not appear altogether impossible of solution. For example, some means of suppressing the dust might be devised. Even partial success in this direction would produce very satisfactory results. The first step has been taken by making use of slag-pockets, although, as pointed out above, these can only be regarded as retaining a very small fraction of the dust which comes through the furnace. It seems quite possible that some method could be found either for preventing a large portion of the dust from entering the checkerwork, or else for removing the dust as it settles on the bricks. Another possible way out of the difficulty consists in replacing the acid bricks of the checkerwork by basic ones. Magnesia bricks are, of course, somewhat expensive, and in many cases are liable to shrink a great deal. There are a number of other basic materials, having the advantage as regards expense, which might quite conceivably furnish very suitable bricks at the cost of a certain amount of research. Bauxite, serpentine, steatite, lime, dolomite, and magnesian limestone may be instanced. Bauxite bricks have, up to now, proved rather troublesome on account of their tendency to shrink, but there is no reason why this weakness should not be overcome by burning at a sufficiently high temperature, and by suitably arranging the texture and composition. The chief difficulty in the case of lime lies in the rapidity with which it absorbs moisture. On the other hand, lime which has been fused in, for instance, an electric furnace, is said to resist water very well. Dolomite and magnesian limestone would seem to be exceptionally good materials to experiment with. Magnesia bricks appear to have proved quite a success for the walls and bottom. They are, however, somewhat expensive, and very often shrink a great deal, with the result that the joints are widened and portions of the brick break away. Another suggestion involves the use of ganister, or good firebricks of minimum porosity, combined with a maximum resistibility against temperature fluctuations. But so long as the bricks are of an acid nature, fluxing will still go on, however dense and free from cracks they are. Furthermore, there will still be difficulties to overcome, which arise out of the dust accumulating in the checkerwork.

# GASES OCCLUDED IN ALLOY STEELS.[1]

By J. W. DONALDSON, B.Sc. (Glasgow).

## INTRODUCTION.

Since Graham (1) in 1865 heated wrought iron *in vacuo* and found the evolved gases to be a mixture of CO, $CO_2$, $H_2$, and $N_2$, many investigations have been carried out on gases occluded in pig irons and steels. Steels have been dealt with, varying both in carbon content and in method of manufacture. So far, no investigations have been carried out on the alloy steels, and the object of the present research is to deal with those types of steel.

Before describing the method of carrying out the research and considering the results obtained, a short summary of the work previously done and of the results obtained with ordinary carbon steels might be considered. Parry (2), whose experiments followed those of Graham, worked on a number of commercial irons and steels. He found that the principal gases evolved were carbon monoxide and hydrogen, the hydrogen predominating at low temperatures. The volumes of the evolved gases being high, however, have always caused his results to be adversely criticised.

The researches of Troost and Hautefeuille (3), published in 1876, followed and confirmed the nature of the dissolved gases, viz. that hydrogen was dissolved in excess of carbon monoxide. They also indicated that cast iron dissolves gases in considerably larger quantity than does steel.

Stead's (5) investigations on the effect which drilling steel under water has on occluded gases, and Müller's (6) on the nature and amount of the gas escaping from steel while in a fluid condition are important. Stead found that a considerable quantity of gas was evolved when a steel was drilled under water or mercury. The volumes of gas obtained varied, and the nature of the gases was slightly different from those

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[1] Received March 12, 1915.

obtained by heating steel *in vacuo.* Müller's work, on the other hand, confirmed that of previous investigations as to the nature of the evolved gases.

Boudouard's ([7]) researches were conducted on merchant iron and iron wire, while Belloc ([8]) dealt with a mild steel (0·12 per cent. carbon) in order to ascertain the relationship between the temperature and the rate of evolution of the gas. The rate of evolution was found to agree with the critical points of the steel. The nature of the evolved gases was in accordance with previous results.

The effect of deoxidisers on the dissolved gases was the object of investigations carried out by Goerens ([10]), samples of steel taken before and after deoxidation being heated *in vacuo* and the evolved gas being collected and examined. The results obtained indicated that certain processes of deoxidising steel increased the volume of dissolved gas.

From 1908 to 1910 Baker ([11]) carried out researches on gases occluded in mild and high carbon steels. He found that the nature of the evolved gases was similar in each of those steels, the carbon content having apparently no effect on the dissolved gases. The maximum evolution of gas occurred at the critical points; reheating the steel had no appreciable effect on the volume of gas evolved, but mechanical operations such as rolling reduced the volume of gas retained by the steels. The evolved gases were chiefly carbon monoxide and hydrogen, carbon dioxide and nitrogen only occurring in small quantities, and constituting not more than 2·5 per cent. of the total gas evolved. Methane was also present in extremely small quantities. Hydrogen was in excess at low temperatures, but diminished in quantity as the temperature rose. The carbon monoxide attained a maximum at 700° C. Above 760° C. carbon monoxide and hydrogen occurred in equal proportions.

The most recent researches on the subject of occluded gases have been the work of Charpy and Bonnerot ([12]) and of Austin ([13]). Charpy and Bonnerot's investigations dealt with the effect of pressure, the quantity of the steel used, and the form (solid or drillings) of the steel, on the volume of the dissolved gases. A number of commercial steels were also examined.

Austin heated cast iron and various commercial steels to their melting points *in vacuo* and collected all the gases evolved from the metal.

In all the above investigations, although many of the results obtained have been at variance and definite conclusions have been difficult to arrive at, one or two points may be taken as more or less generally accepted. These may be summarised as follows:

1. Wrought iron, cast iron, and steel dissolve gases in varying quantities, those gases being CO, $CO_2$, $H_2$, $N_2$, and $CH_4$.
2. In steel the principal dissolved gases are CO and $H_2$. $H_2$ predominates at low temperature, diminishes to a minimum as the temperature increases, but slightly increases on still further heating. CO is at a minimum at low temperatures, increases to a maximum, and then slightly decreases. Both gases are present in more or less equal proportions at high temperatures. $CO_2$, $CH_4$, and $N_2$ only occur in small quantities, and do not as a rule exceed 5 per cent. of the total gas evolved.
3. Cast iron dissolves more gas than steel.
4. Drilling steel under water or mercury liberates a considerable amount of gas.
5. Reheating a steel does not affect the volume or nature of the dissolved gas.
6. Mechanical work such as rolling or forging decreases the volume of dissolved gas.
7. The rate of evolution of a gas from a steel has a relation with its critical points, the largest amount being evolved at the critical points.

## OBJECTS OF THE RESEARCH.

The object of the present research, as previously mentioned, is an investigation of the gases occluded by the various alloy steels. The chief points it was sought to investigate were:

1. The nature and volume of the gases evolved when the steels are heated *in vacuo*.

2. The relationship, if any, which exists between the percentage of the special element present and the nature and evolution of the gas.
3. The relationship, if any, which exists between the critical points and the nature and evolution of the gas.

The alloy steels dealt with in the present report are nickel, silicon, chromium, and manganese steels.

## APPARATUS.

The steels, in the form of coarse drillings contained in a porcelain boat, were introduced into a porcelain tube glazed internally and externally. One end of the tube was connected to a three-fall Sprengel pump and a McLeod gauge, while the other end entered a platinum platinum-iridium thermocouple enclosed in a silica tube. The porcelain tube was heated by a gas-fired furnace.

A general sketch of the apparatus is shown in Fig. 1.

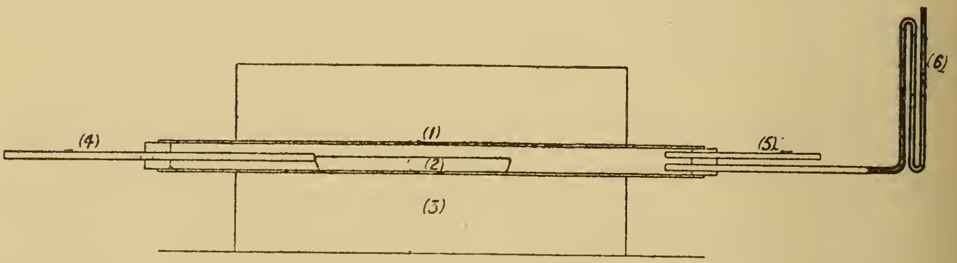

FIG. 1.

Porcelain tube. (2) Boat. (3) Furnace. (4) Silica tube for thermocouple. (5) To three-fall Sprengel pump. (6) McLeod gauge.

## STEELS.

The composition of the steels investigated was as follows:

| | Nickel. | Silicon. | Chromium. | Manganese. |
|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| Carbon . . . . . | 0·21 | 0·21 | 0·43 | 0·08 |
| Silicon . . . . . | 0·084 | 3·46 | 0·32 | 0·13 |
| Manganese . . . . | 0·72 | 0·29 | 0·25 | 3·50 |
| Nickel . . . . . | 3·20 | ... | ... | ... |
| Chromium . . . . | ... | ... | 3·28 | ... |

The above steels were obtained having, as nearly as possible, a similar percentage of the special element in order to ascertain what effect, if any, the various special elements had on the nature and evolution of the evolved gases. The carbon content varies. This should have a slight effect on the volume of the gases, but no appreciable effect on the nature of the gases.

As regards the condition of the steels, the nickel steel was rolled, the silicon, chromium, and manganese steels being forged.

The samples heated were in the form of coarse drillings, care being taken in the drilling to prevent contamination from oil and other sources.

## METHOD OF WORKING.

Before proceeding with the examination of the steels, the apparatus was thoroughly tested in order to make quite certain of the impermeability of the tube to furnace gases, and also to ensure the complete removal of any occluded air or gas in the material of the tube. It was found that on heating to 900° C. for seven hours per day, the amount of gas evolved was a constant quantity of 1 cubic centimetre per week. A quantity was collected, and on examination was found to have the following composition:

| | Per Cent. |
|---|---|
| $CO_2$ | 14·21 |
| $CO$ | 9·76 |
| $H_2$ | 65·41 |
| $CH_4$ | 9·42 |
| $N_2$ | 1·20 |
| | 100·0 |

This quantity was so small that it was thought unnecessary to make a correction for it in the analyses.

After the steel was introduced, the tube was exhausted and allowed to stand for twenty-four hours before beginning to collect the gases. To remove the film of air still clinging to the tube it was necessary to heat it to 300° C. The air was rapidly evolved and its composition shown by analysis.

As no appreciable amount of gas was evolved below 500° C., this temperature was taken as the initial temperature of

TABLE I.—*Nickel Steel* (*25 grammes*).

| Temperature of Heating. | Duration of Heating. | Volume of Gas in Cubic Centimetres (at N.T.P.). | $CO_2$ per Cent. | CO per Cent. | $H_2$ per Cent. | $CH_4$ per Cent. | $N_2$ per Cent. | Remarks. |
|---|---|---|---|---|---|---|---|---|
| 500° C. | 7 hours | 4·2 | 1·29 | 2·22 | 95·79 | 0·23 | 0·47 | Very slow evolution of gas. Exhausted in four hours. |
| 570° C. | 7 hours | 9·3 | 0·65 | 37·66 | 61·17 | 0·39 | 0·13 | Slow evolution of gas. Exhausted in five hours. |
| 616° C.[1] | 7 hours | 13·3 | 1·00 | 50·33 | 48·16 | 0·33 | 0·18 | Rapid evolution of gas. Exhausted in six hours. |
| 652° C.[2] | 7 hours | 8·4 | 0·57 | 74·57 | 24·52 | 0·22 | 0·12 | Slow evolution of gas. Exhausted in five hours. |
| 684° C.[3] | 7 hours | 10·3 | 0·48 | 60·72 | 38·19 | 0·36 | 0·25 | Rapid evolution of gas. Exhausted in five hours. |
| 782° C. | 7 hours | 9·3 | 0·58 | 47·31 | 51·41 | 0·39 | 0·31 | Slow evolution of gas. Exhausted in five hours. |
| 880° C. | 7 hours | 6·7 | 0·60 | 51·31 | 47·64 | 0·22 | 0·23 | Very slow evolution of gas. Exhausted in four hours. |
| Average composition . . . . | | | 0·74 | 46·30 | 52·41 | 0·31 | 0·24 | |

[1] Ar1 maximum.

[2] Ar3 maximum.

[3] Ar2 maximum.

TABLE II.—*Silicon Steel* (40 *grammes*).

| Temperature of Heating. | Duration of Heating. | Volume of Gas in Cubic Centimetres (at N.T.P.). | $CO_2$ per Cent. | CO per Cent. | $H_2$ per Cent. | $CH_4$ per Cent. | $N_2$ per Cent. | Remarks. |
|---|---|---|---|---|---|---|---|---|
| 500° C. | 7 hours | 5·1 | 1·46 | 3·64 | 94·54 | 0·24 | 0·12 | Very slow evolution of gas. Exhausted in four hours. |
| 600° C. | 7 hours | 8·1 | 0·33 | 7·96 | 91·46 | 0·17 | 0·08 | Slow evolution of gas. Exhausted in five hours. |
| 700° C.[1] | 7 hours | 10·7 | 0·26 | 41·16 | 58·21 | 0·26 | 0·11 | Rapid evolution of gas. Exhausted in six hours. |
| 750° C. | 7 hours | 10·2 | 0·59 | 53·13 | 45·79 | 0·29 | 0·20 | Rapid evolution of gas. Exhausted in six hours. |
| 767° C.[2] | 7 hours | 9·6 | 1·18 | 54·27 | 44·10 | 0·27 | 0·18 | Slow evolution of gas. Exhausted in five hours. |
| 800° C.[1] | 7 hours | 6·8 | 1·39 | 53·87 | 44·16 | 0·35 | 0·23 | Slow evolution of gas. Exhausted in five hours. |
| 880° C. | 7 hours | 5·0 | 2·11 | 49·04 | 48·06 | 0·30 | 0·52 | Very slow evolution of gas. Exhausted in four hours. |
| Average composition . . . . | | | 1·05 | 37·59 | 60·90 | 0·27 | 0·19 | |

[1] Critical range.

[2] Maximum point of range.

TABLE III.—*Chromium Steel* (40 *grammes*).

| Temperature of Heating. | Duration of Heating. | Volume of Gas in Cubic Centimetres (at N.T.P.). | $CO_2$ per Cent. | CO per Cent. | $H_2$ per Cent. | $CH_4$ per Cent. | $N_2$ per Cent. | Remarks. |
|---|---|---|---|---|---|---|---|---|
| 500° C. | 7 hours | 5·1 | 2·11 | 18·21 | 78·84 | 0·32 | 0·52 | Slow evolution of gas. Exhausted in four hours. |
| 600° C. | 7 hours | 7·3 | 2·52 | 27·72 | 68·78 | 0·25 | 0·73 | Rapid evolution of gas. Exhausted in six hours. |
| 700° C.[1] | 7 hours | 7·6 | 0·91 | 40·16 | 58·25 | 0·15 | 0·53 | Rapid evolution of gas. Exhausted in six hours. |
| 750° C. | 7 hours | 6·4 | 1·53 | 52·69 | 44·92 | 0·33 | 0·53 | Slow evolution of gas. Exhausted in five hours. |
| 775° C.[2] | 7 hours | 6·1 | 1·38 | 62·31 | 35·62 | 0·23 | 0·46 | Slow evolution of gas. Exhausted in five hours. |
| 800° C.[1] | 7 hours | 5·9 | 2·58 | 62·92 | 33·58 | 0·33 | 0·59 | Slow evolution of gas. Exhausted in four hours. |
| 880° C. | 7 hours | 3·6 | 2·41 | 49·96 | 46·89 | 0·33 | 0·41 | Very slow evolution of gas. Exhausted in four hours. |
| Average composition . . . . | | | 1·92 | 44·85 | 52·41 | 0·28 | 0·54 | |

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[1] Critical range.

[2] Maximum point of range.

TABLE IV.—*Manganese Steel* (40 grammes).

| Temperature of Heating. | Duration of Heating. | Volume of Gas in Cubic Centimetres (at N.T.P.) | $CO_2$ per Cent. | CO per Cent. | $H_2$ per Cent. | $CH_4$ per Cent. | $N_2$ per Cent. | Remarks. |
|---|---|---|---|---|---|---|---|---|
| 500° C. | 7 hours | 4·6 | 2·66 | 10·13 | 86·31 | 0·53 | 0·37 | Very slow evolution of gas. Exhausted in four hours. |
| 537° C.[1] | 7 hours | 6·5 | 1·53 | 15·42 | 82·44 | 0·38 | 0·23 | Slow evolution of gas. Exhausted in six hours. |
| 600° C. | 7 hours | 5·8 | 2·33 | 32·17 | 65·00 | 0·25 | 0·25 | Slow evolution of gas. Exhausted in five hours. |
| 700° C. | 7 hours | 5·2 | 0·91 | 51·09 | 47·45 | 0·26 | 0·29 | Slow evolution of gas. Exhausted in four hours. |
| 800° C. | 7 hours | 4·5 | 1·99 | 65·63 | 31·60 | 0·33 | 0·45 | Very slow evolution of gas. Exhausted in four hours. |
| 880° C. | 7 hours | 3·0 | 2·21 | 48·15 | 48·89 | 0·37 | 0·38 | Very slow evolution of gas. Exhausted in three hours. |
| Average composition . . . . | | | 1·94 | 37·10 | 60·28 | 0·35 | 0·33 | |

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[1] Critical range maximum.

TABLE V.—*Cubic Centimetres per* 100 *Grammes of Steel.*

| Nickel Steel. | | Silicon Steel. | | Chromium Steel. | | Manganese Steel. | |
|---|---|---|---|---|---|---|---|
| 0·21 per Cent. Carbon. | 3·20 per Cent. Nickel. | 0·21 per Cent. Carbon. | 3·46 per Cent. Silicon. | 0·43 per Cent. Carbon. | 3·28 per Cent. Chromium. | 0·08 per Cent. Carbon. | 3·50 per Cent. Manganese. |
| Degrees C. | Cubic Cms. | Degrees C. | Cubic Cms. | Degrees C. | Cubic Cms. | Degrees C. | Cubic Cms. |
| 500 | 16·8 | 500 | 12·7 | 500 | 12·7 | 500 | 11·5 |
| 570 | 37·2 | 600 | 20·3 | 600 | 18·3 | 537 | 16·3 |
| 616 | 53·2 | 700 | 26·7 | 700 | 19·0 | 600 | 14·5 |
| 652 | 33·6 | 750 | 25·5 | 750 | 16·0 | 700 | 13·0 |
| 684 | 41·2 | 767 | 24·0 | 775 | 15·2 | 800 | 11·2 |
| 782 | 37·2 | 800 | 17·0 | 800 | 14·8 | 880 | 7·5 |
| 880 | 26·8 | 880 | 12·5 | 880 | 9·0 | ... | ... |
| Total . . | 246·0 | Total . . | 138·7 | Total . . | 105·0 | Total . . | 73·9 |
| 2·46 cubic cms. per gramme. | | 1·39 cubic cms. per gramme. | | 1·05 cubic cms. per gramme. | | 0·74 cubic cm. per gramme. | |

heating. Heating was also maintained at various temperatures covering the critical ranges of the steels. The final temperature of heating in each case was 880° C. In most cases the gas was completely evolved at each temperature in from five to six hours, but for uniformity a period of seven hours' heating was maintained. The rate of evolution of the gas was observed by the movement of the mercury in the McLeod gauge.

## CONSIDERATION OF THE RESULTS.

In considering the results the first point to be noted is the volumes of the gas evolved from the various steels.

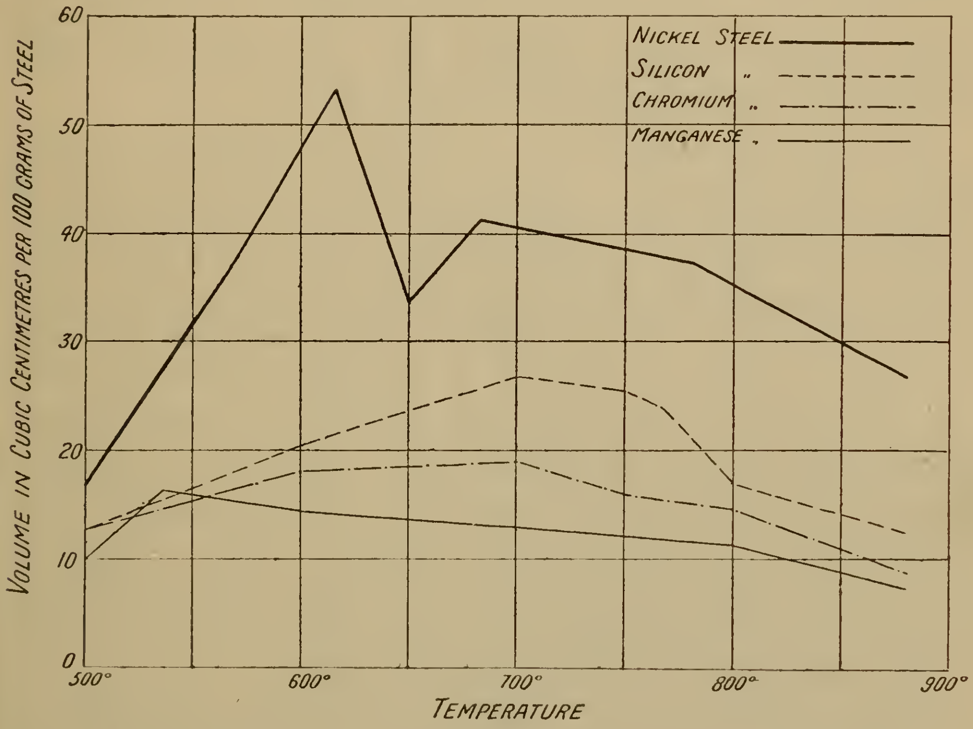

FIG. 2.

Referring to Table V. or Fig. 2, it is seen that the largest amount of gas is obtained from the nickel steel, the volumes obtained from the silicon, chromium, and manganese steels diminishing in the order given. Compared with the results obtained in some previous investigations on ordinary carbon steels, the volumes are high. This may be due to the fact that the steels dealt with were not specially prepared steels, but ordinary commercial steels. The nickel steel is an acid open-hearth steel, the others crucible or side blown converter steels. It would have been interesting and instructive to have compared the results obtained with those which would be obtained from carbon steels prepared by similar processes. Time did not permit this being carried out for the present report, but such material has already been obtained and its examination commenced.

The nature of the gases obtained from the various steels offers some interesting considerations. In general carbon monoxide and hydrogen predominate in the evolved gases, carbon monoxide at high temperatures and hydrogen at low temperatures. This is in accordance with previous investigations: carbon dioxide, methane, and nitrogen, in all cases, being less than 2·5 per cent. of the total gas.

The average composition of the gas evolved from the nickel and chromium steels is similar to those given by Baker for high and low carbon steels. His results for a mild steel containing 0·13 per cent. carbon were 1·17 per cent. $CO_2$, 45·64 per cent. CO, 52·12 per cent. $H_2$, 0·72 per cent. $CH_4$, 0·37 per cent. $N_2$. In the silicon and manganese steels the amount of carbon monoxide is decreased by about 8 to 10 per cent. and the hydrogen increased correspondingly. This would appear to indicate that silicon and manganese decrease the solubility of steel for carbon monoxide while increasing its solubility for hydrogen. The amount of nitrogen in the chromium steel, although not exceptionally high, is distinctly higher than in the other steels and shows little variation at the different temperatures.

With regard to the evolution of the carbon monoxide and the hydrogen, each of the steels might be considered separately.

1. In the nickel steel, carbon monoxide is present in small quantity at 500° C. At 570° C., however, it has increased by 35 per cent., and continues to increase until it attains a maximum at 652° C. It then decreases, reaching a minimum at 782° C., and then again increases slightly. The variation of the hydrogen

is the reverse of the carbon monoxide, the maximum points of the former being the minimum points of the latter and *vice versa.*

2. The evolution of the carbon monoxide from the silicon steel is different. Although in slightly larger amount at 500° C., it does not show a marked increase at 600° C., 700° C. being the temperature where the increase takes place. The maximum evolution is obtained at 767° C., from which temperature it decreases to a minimum at 880° C. The hydrogen occurs in the reverse manner.
3. The percentage of carbon monoxide in the chromium steel is much higher at 500°, and its increase is gradual, no sudden increases being apparent. In this it differs from the nickel and silicon steels. The carbon monoxide shows a maximum and the hydrogen a minimum at 800° C.
4. The manganese steel behaves in a manner similar to the chromium steel, the carbon monoxide attaining its maximum and the hydrogen its minimum at 800° C. The increase and decrease of the two gases respectively are regular.

Considering finally the rate of evolution of the gases in the nickel steel the largest amounts are evolved in the neighbourhood of the $Ar_1$ and $Ar_3$ points, and similarly in the manganese steel, the largest amount is evolved in the region of the maximum point of the critical range. The silicon and chromium steels yield the largest volumes of gas at temperatures covering the whole of the critical ranges.

The general conclusions which may be drawn from the above are:

(*a*) The volume of the gas dissolved in alloy steels diminishes, according as the special element is nickel, silicon, chromium, or manganese.

(*b*) The nature of the occluded gases is similar to those of ordinary steel, except that silicon and manganese decrease the amount of carbon dioxide present while increasing the amount of hydrogen. Chromium tends slightly to increase the amount of nitrogen. The evolution of the carbon monoxide and hydrogen varies for the different alloy steels.

(*c*) The largest quantities of gas are evolved in the neighbourhood of the critical points or over the critical ranges, agreeing with ordinary carbon steels in this respect.

The investigations were carried out by the author in the metallurgical laboratories of the Royal Technical College, Glasgow. His thanks are due to Professor Campion for his kindly advice and interest, and to Sir R. A. Hadfield, Sheffield, and Mr. David Colville, Motherwell, for samples of the various steels.

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# AN INVESTIGATION OF LIQUID CONTRACTION IN CAST IRON.[1]

## PART II.

By GEORGE HAILSTONE (Smethwick).

In a Carnegie memoir presented by the present author in 1913, liquid contraction in cast iron of fairly good quality was dealt with. The following were the conclusions arrived at as a result of that investigation:

1. Liquid contraction is accompanied by a lowering of the specific gravity or density.
2. Casting temperature is one of the ruling factors in obtaining a dense and solid casting, and therefore also affects the liability to liquid contraction.
3. When castings have been cast with iron hotter than will conduce to liquid contraction, solid and dense castings result; when cast with iron too cold to conduce to liquid contraction, blowholes appear. Hence the casting hot gives dense castings, medium heat gives liquid contraction, and cold iron gives blowholes.
4. The more regular the sizes of the microscopical constituents the less will be the liquid contraction.
5. Conditions which conduce to a maximum solid contraction conduce to a maximum liquid contraction.
6. Gases appear to be held in more intimate contact in cast iron poured at a high temperature, and therefore tend to produce a more solid and dense casting.

Since the publication of the above, and by the kindness of the Carnegie Scholarship Committee, who awarded an additional grant in 1914, the author has been able to extend his

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[1] Manuscript received April 1, 1915.

investigations on cast iron of commoner variety, the results of which are embodied in the following report.

The results obtained will be presented in the following order:—

Preparation of samples.
Casting temperatures.
Analysis and specific gravity of samples.
Tensile strength.
Appearance of fractured surfaces.
Size of microscopic constituents.
Hardness of samples.
Microstructure.
Gases evolved on heating the specimens for twelve hours at a temperature of 950° C.

### General Scheme.

The methods of moulding the test-bars, measurement of the micro-constituents, specific gravity, hardness, and chemical analysis were those used in the previous investigation.

The K test-bars being cast in duplicate in each case, one only being used in the above tests, the long leg of the other was used for the tensile test, the bar being turned to 0·25 square inch in cross-section with 2 inches parallel.

## THE AUTHOR'S RESEARCH.

### Preparation of Samples.

Ten sets of bars were moulded in 12-inch square moulding-boxes, with facing sand as usually used for green-sand work. Great care was taken to insure, as far as possible, that the moulds and methods of running were the same in each case, the down and in gates being of the same size each time.

The ten moulds were placed side by side and cast, at intervals of two minutes between each, from a ladle containing 5 cwt. of iron tapped from the cupola.

The casting temperature was taken by means of a thermo-couple and a milli-voltmeter, the thermo-couple being held in the ladle of metal during the pouring, and the reading of the millivoltmeter being taken as soon as each mould was full.

The intervals of time between the casting of the ten bars and the temperature of casting is given in Table I.

After being cast the castings were allowed to stay in the moulds until next day, when they were fettled, and then broken through the line marked A—B in Fig. 1 for examination.

The analysis and specific gravity of each of the bars is shown in Table II.

From these analyses it will be seen that the total carbon in the whole series is practically constant, the bar cast last only containing a few hundredths of a per cent. more than the bar cast first. The combined carbon, however, differs considerably, being greatest in the No. 1 bar and gradually decreasing in the other bars with the reduction of the casting temperature. The silicon is practically constant through the series, as is also the phosphorus. An interesting feature of the series is that No. 1 bar contains nearly double the amount of manganese than do the others, also the sulphur is much higher. This is no doubt due to the top layer of metal in the ladle containing an excess of manganese sulphide, besides which the metal was at the proper temperature for the elimination of manganese sulphide.

From an observation of the specific gravity of the bars it will be noticed the bar cast at the highest temperature has the highest density, the density diminishing as the casting temperature becomes lower in the subsequent bars.

## TENSILE STRENGTH OF THE BARS.

Table III. gives the tensile test results together with the casting temperatures of the ten bars.

It is very interesting to see that the bars cast at high temperatures yield the highest results, the strength decreasing with a reduction of the casting temperature. It will be noted the best results are obtained in bars Nos. 1 to 4, which have casting temperatures of from 1428° C. to 1386° C., a range in temperature of 42° C. for this particular class of iron. The

TABLE I.

| Bar. | Time Cast. | Casting Temperature. Degrees C. | Interval in Minutes between the Casting of "K" Bars after Bar No. 1. |
|---|---|---|---|
| | H. M. | | |
| 1 | 3 30 | 1428 | ... |
| 2 | 3 32 | 1400 | 2 |
| 3 | 3 34 | 1390 | 4 |
| 4 | 3 36 | 1386 | 6 |
| 5 | 3 38 | 1361 | 8 |
| 6 | 3 40 | 1348 | 10 |
| 7 | 3 42 | 1330 | 12 |
| 8 | 3 44 | 1302 | 14 |
| 9 | 3 46 | 1272 | 16 |
| 10 | 3 48 | 1264 | 18 |

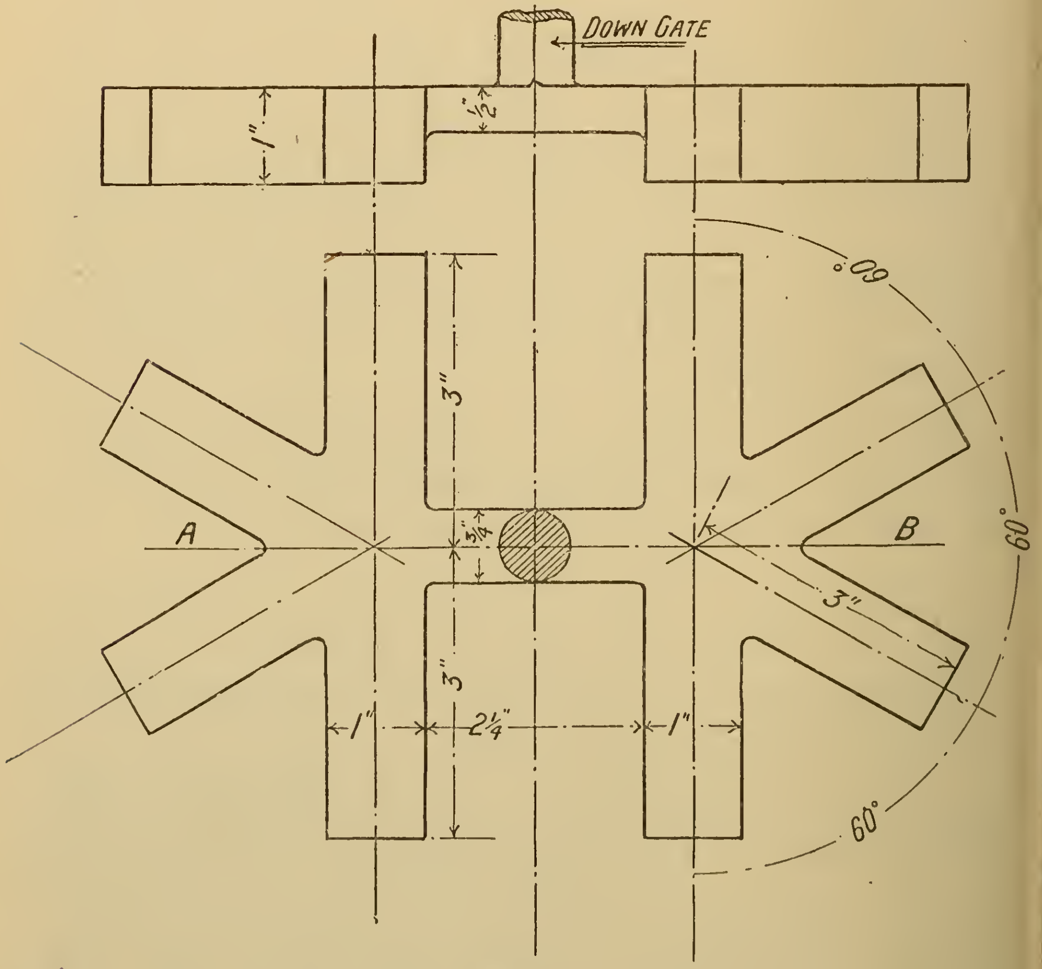
DOWN GATE
1"
½"
3"
60°
60°
60°
A
B
¾"
3"
3"
1"
2¼"
1"

FIG. 1.

TABLE II.—*Analysis of Samples.*

| Chemical Constituents. | Bars. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
| Total carbon . . . . . | 3·258 | 3·246 | 3·261 | 3·256 | 3·281 | 3·283 | 3·291 | 3·295 | 3·305 | 3·312 |
| Graphitic carbon . . . . | 2·830 | 2·840 | 2·862 | 2·891 | 2·915 | 2·926 | 2·951 | 2·987 | 3·012 | 3·126 |
| Combined carbon . . . . | 0·428 | 0·406 | 0·399 | 0·365 | 0·366 | 0·357 | 0·340 | 0·308 | 0·293 | 0·186 |
| Silicon . . . . . . | 1·907 | 1·875 | 1·900 | 1·898 | 1·894 | 1·904 | 1·915 | 1·901 | 1·902 | 1·910 |
| Sulphur . . . . . . | 0·114 | 0·097 | 0·092 | 0·096 | 0·096 | 0·094 | 0·094 | 0·093 | 0·093 | 0·092 |
| Phosphorus . . . . . | 1·482 | 1·414 | 1·408 | 1·412 | 1·441 | 1·441 | 1·460 | 1·471 | 1·469 | 1·469 |
| Manganese . . . . . | 0·420 | 0·270 | 0·270 | 0·265 | 0·268 | 0·268 | 0·267 | 0·265 | 0·266 | 0·264 |
| Specific gravity of bars . . . | 7·281 | 7·262 | 7·240 | 7·225 | 7·201 | 7·158 | 7·123 | 7·085 | 7·012 | 6·936 |

difference in strength between No. 1 bar and No. 10 bar is most marked, a reduction of 164° C. in casting temperature reducing the tensile strength by more than 50 per cent.

Transverse microsections were cut from the tensile bars for microscopic analysis; this subject will, however, be dealt with later.

Table III.

| Bar No. | Tensile Strength in Tons per Square Inch. | Casting Temperature. Degrees C. |
|---|---|---|
| 1 | 10·98 | 1428 |
| 2 | 10·94 | 1400 |
| 3 | 10·87 | 1390 |
| 4 | 10·50 | 1386 |
| 5 | 9·64 | 1361 |
| 6 | 9·60 | 1348 |
| 7 | 8·40 | 1330 |
| 8 | 7·65 | 1302 |
| 9 | 6·42 | 1272 |
| 10 | 5·24 | 1264 |

## Appearance of the Fractured Surfaces.

The appearance of the fractured surfaces of the K bars is shown in Fig. 2, Plate VI.

Bars Nos. 1 to 5 exhibit the fracture of a close-grained solid cast iron of a light grey colour. Bars Nos. 5 and 6 show a slight opening of the grain at the centre, the colour being of a shade darker grey than in the previous bars, whilst bars 8, 9, and 10 exhibit excessive openness in the centre, and blowholes will be noticed to appear, being small in bar 8 and gradually increasing in size to a maximum in bar No. 10, bars Nos. 8, 9, and 10 also showing increasing depths of greyness in colour.

## Size of Microscopical Constituents.

On polishing the sections for the measurement of the microscopical constituents it was found that bars Nos. 1, 2, 3, 4 and 5 exhibited an even surface and were of a sound nature, therefore only one set of readings was taken, whilst bars

Nos. 6 and 7 showed signs of liquid contraction, a large contraction hole being present in No. 7. Bars Nos. 8, 9, and 10 exhibited liquid contraction also, blowholes being least in No. 8, larger in No. 9, and reaching a maximum in No. 10. Readings were taken from both the unaffected or sound areas and the affected or unsound areas in the case of the bars Nos. 6 to 10.

Table IV. gives the mean dimensions of the constituents from twelve readings in each case. It will be observed that bar No. I. has the highest density of the series, contains the smallest and thinnest flakes and plates of graphite and the largest areas of manganese sulphide.

The size of the flakes and plates of graphite in the bars increases as their identification numbers, the areas of manganese sulphide diminishing in size.

With regard to bars Nos. 6 to 10 it will be noticed that in each case the graphite flakes and plates are larger in the affected area than in the unaffected area, whilst the size of the manganese sulphide areas does not vary greatly in the different portions of the same section.

Fig. 3, Plate VII., shows the appearance of the polished surfaces of the bars used for the measurement of the microscopical constituents.

## Hardness of Samples.

The hardness of the samples was determined by the Shore scleroscope, the diameter of the indentation being measured by means of the microscope micrometer. The results are quoted in Table V.

From the hardness numbers obtained by the scleroscope it would be inferred that the ten samples were of approximately the same hardness, but on observing the diameter of the indentation it will be noticed that different diameters are obtained which bear a relation to the specific gravity and casting temperature of the samples. The higher the casting temperature and specific gravity of the sample, the smaller the diameter of the indentation.

TABLE IV.—*Size of Microscopical Constituents.*

| | *Unaffected Area.* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample. | Flakes of Graphite. | | Plates of Graphite. | | | Manganese Sulphide Areas. | | |
| | Length in Inches. | Breadth in Inches. | Length in Inches. | Breadth in Inches. | Area in Square Inches. | Length in Inches. | Breadth in Inches. | Area in Square Inches. |
| 1 | 0·00238 | 0·000032 | 0·00065 | 0·00087 | 0·0000005655 | 0·00065 | 0·00072 | 0·0000004680 |
| 2 | 0·00289 | 0·000038 | 0·00152 | 0·00076 | 0·0000011552 | 0·00063 | 0·00068 | 0·0000004284 |
| 3 | 0·00296 | 0·000039 | 0·00098 | 0·00095 | 0·0000009310 | 0·00054 | 0·00060 | 0·0000003240 |
| 4 | 0·00312 | 0·000046 | 0·00086 | 0·00098 | 0·0000008428 | 0·00042 | 0·00054 | 0·0000002268 |
| 5 | 0·00316 | 0·000048 | 0·00106 | 0·00087 | 0·0000009222 | 0·00041 | 0·00046 | 0·0000001886 |
| 6 | 0·00361 | 0·000057 | 0·00098 | 0·00095 | 0·0000009408 | 0·00035 | 0·00042 | 0·0000001470 |
| 7 | 0·00371 | 0·000071 | 0·00095 | 0·00125 | 0·0000011875 | 0·00027 | 0·00034 | 0·0000000918 |
| 8 | 0·00384 | 0·000079 | 0·00099 | 0·00106 | 0·0000010494 | 0·00024 | 0·00028 | 0·0000000672 |
| 9 | 0·00394 | 0·000086 | 0·00126 | 0·00087 | 0·0000010962 | 0·00019 | 0·00021 | 0·0000000399 |
| 10 | 0·00395 | 0·000098 | 0·00135 | 0·00125 | 0·0000016875 | 0·00015 | 0·00016 | 0·0000000240 |
| | *Affected Area.* | | | | | | | |
| 6 | 0·00586 | 0·000064 | 0·00176 | 0·00123 | 0·0000021648 | 0·00033 | 0·00034 | 0·0000001122 |
| 7 | 0·00652 | 0·000058 | 0·00198 | 0·00132 | 0·0000026136 | 0·00028 | 0·00021 | 0·0000000588 |
| 8 | 0·00786 | 0·000089 | 0·00216 | 0·00146 | 0·0000031536 | 0·00029 | 0·00020 | 0·0000000580 |
| 9 | 0·00854 | 0·000098 | 0·00208 | 0·00145 | 0·0000030160 | 0·00025 | 0·00019 | 0·0000000475 |
| 10 | 0·01526 | 0·000126 | 0·00314 | 0·00214 | 0·0000067196 | 0·00013 | 0·00016 | 0·0000000208 |

TABLE V.

| Sample. | Hardness No. (Shore). Mean of Twelve Determinations. | Diameter of Indentation. Mean of Twelve Determinations. |
|---|---|---|
| | | Inches. |
| 1 | 26 | 0·01589 |
| 2 | 27 | 0·01601 |
| 3 | 26 | 0·01625 |
| 4 | 26 | 0·01728 |
| 5 | 26 | 0·01796 |
| 6 | 26 | 0·01854 |
| 7 | 26 | 0·01926 |
| 8 | 27 | 0·01987 |
| 9 | 26·25 | 0·02126 |
| 10 | 27 | 0·02315 |

The following two diagrams, Figs. 4 and 5, show the Shore hardness number plotted against the specific gravity or density

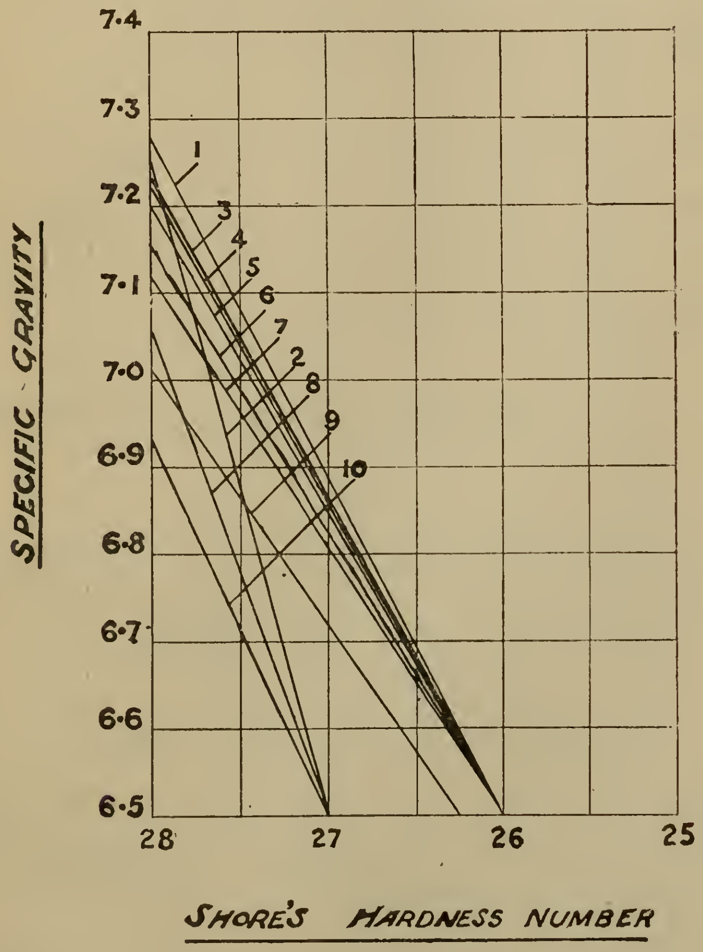

FIG. 4.

of the sample, and the diameter of the indentation plotted against the density.

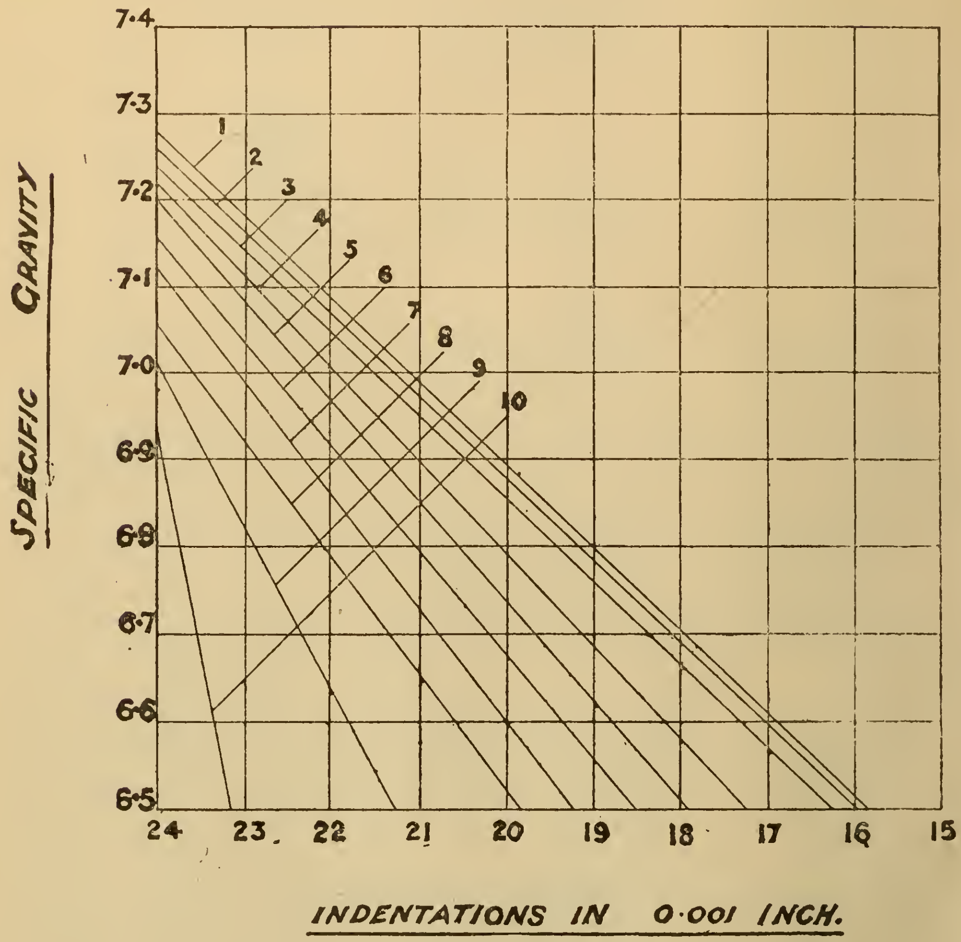

FIG. 5.

As in the previous investigation, it will be noticed that the Shore number does not bear any direct ratio to the density, although the diameter of the indentation does.

## MICROSTRUCTURE OF SAMPLES.

A transverse section was cut from the tensile test-bars of the samples, polished, etched with a 5 per cent. solution of sulphurous acid, and examined under a magnification of 120 diameters.

The bars Nos. 1 to 6 exhibited a close structure, consisting

PLATE VI

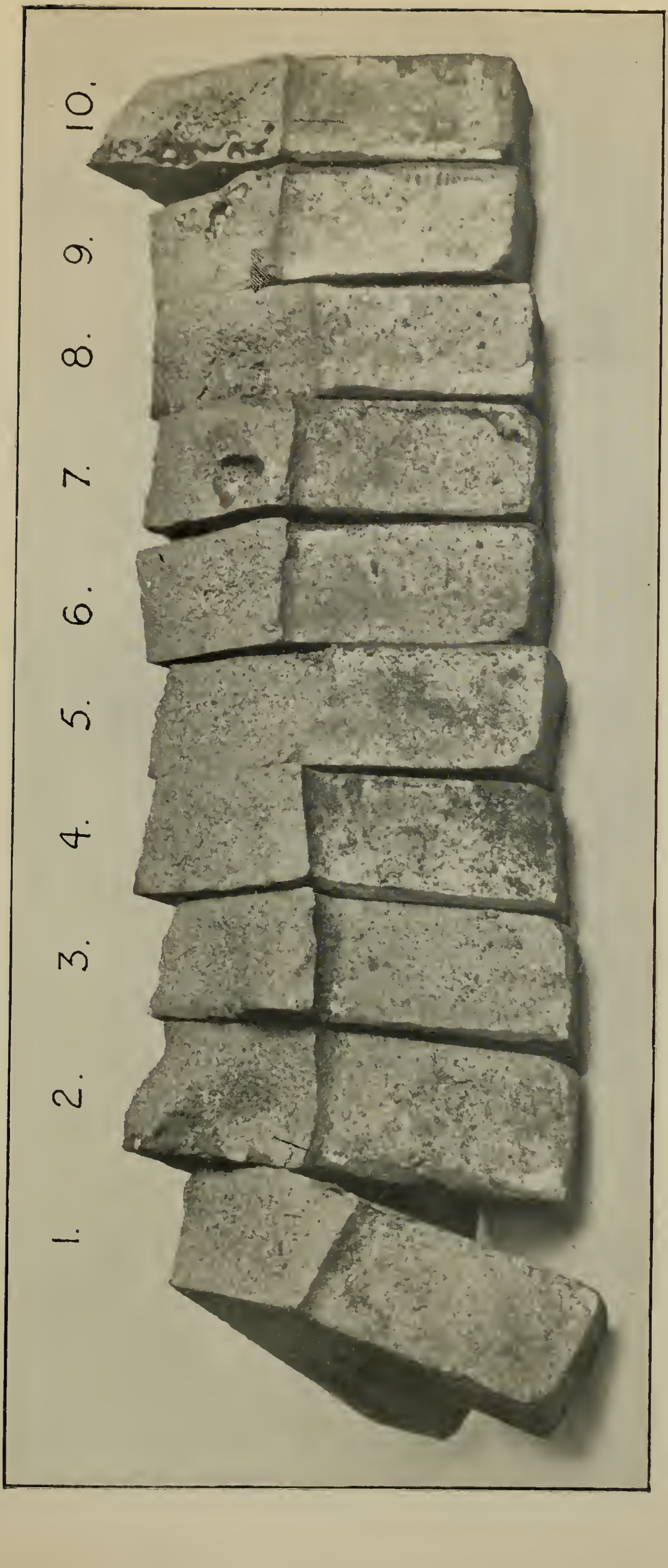
1.
2.
3.
4.
5.
6.
7.
8.
9.
10.

Fig. 2.—Fractured Surfaces of K-bars.

PLATE VII

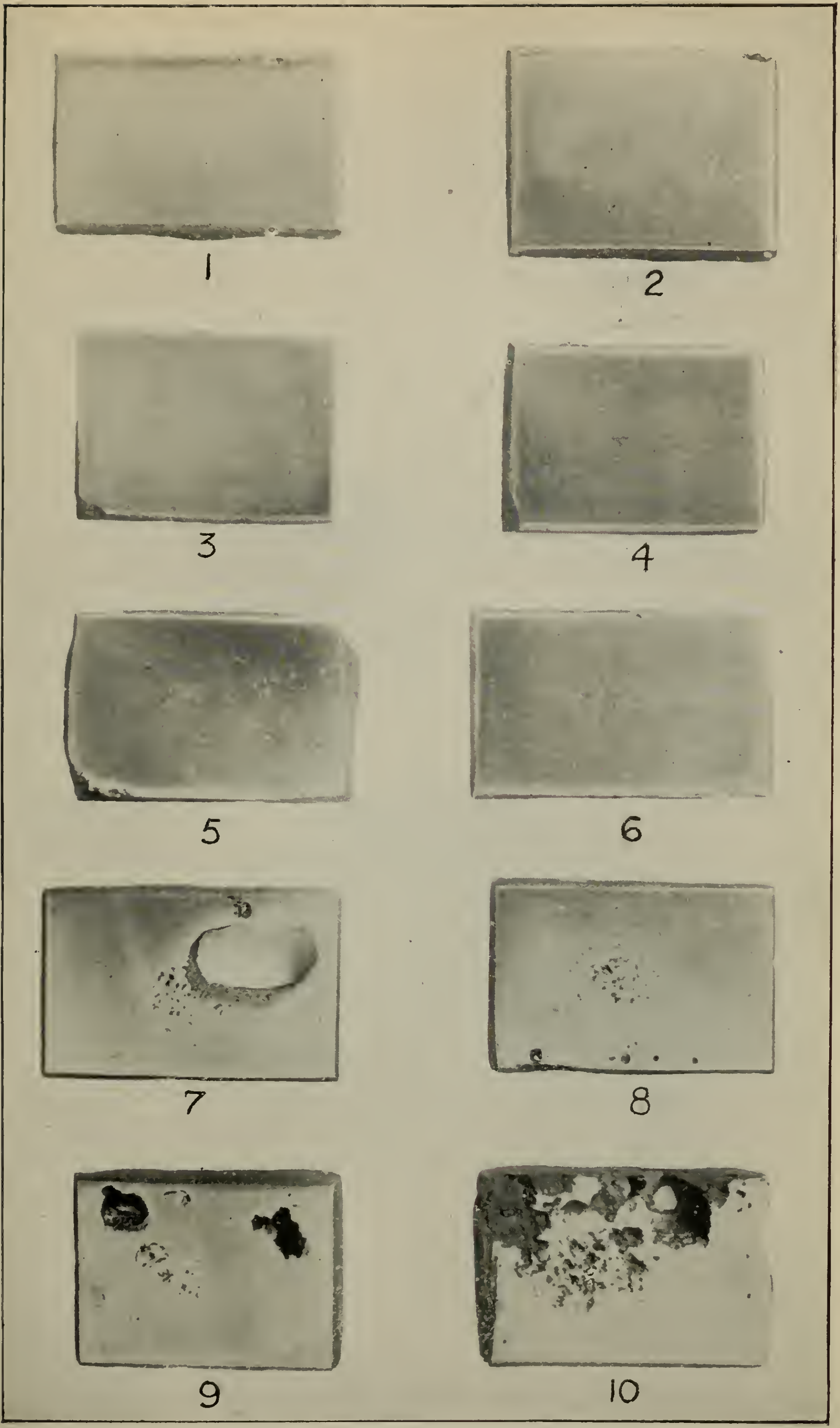
1
2
3
4
5
6
7
8
9
10

FIG. 3.—Polished Surfaces of Bars.

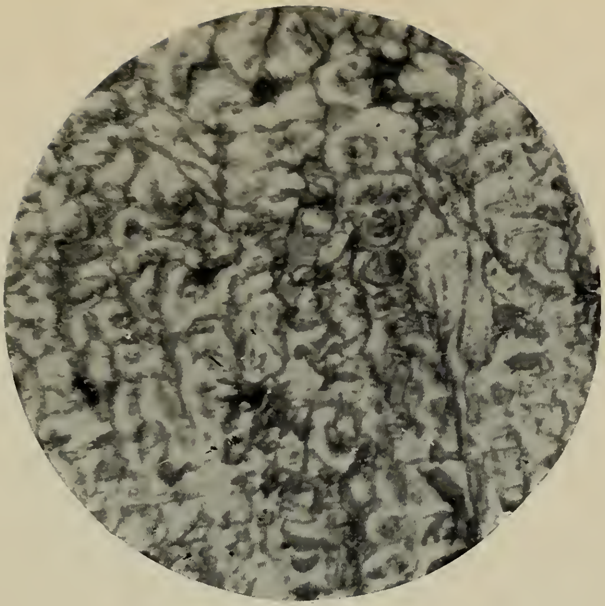

FIG. 6.—Typical Structure exhibited by Samples.

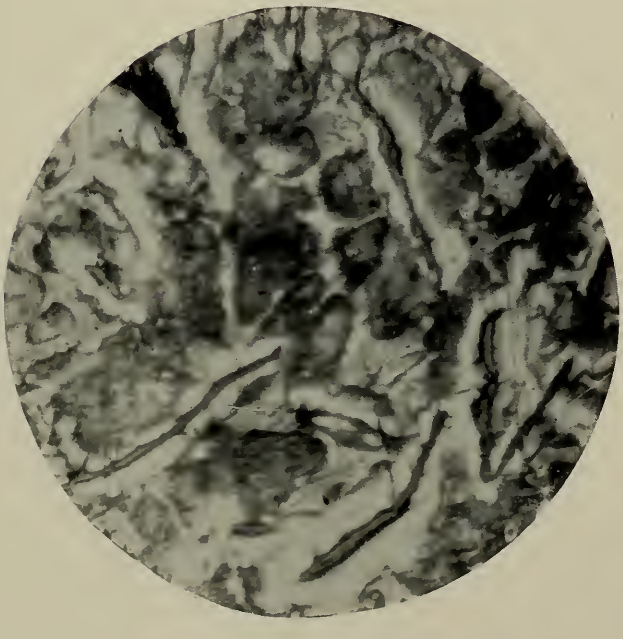

FIG. 7.—Structure of Bar No. 10.

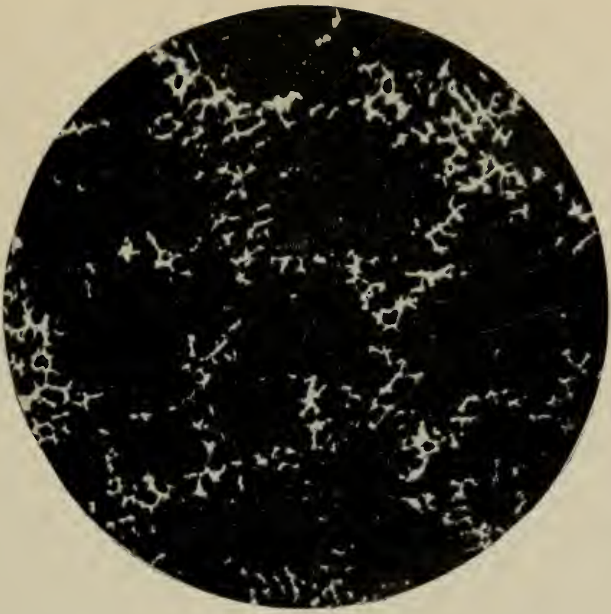

FIG. 8.—Etched Section of Bar No. 1, showing Phosphide Eutectic.

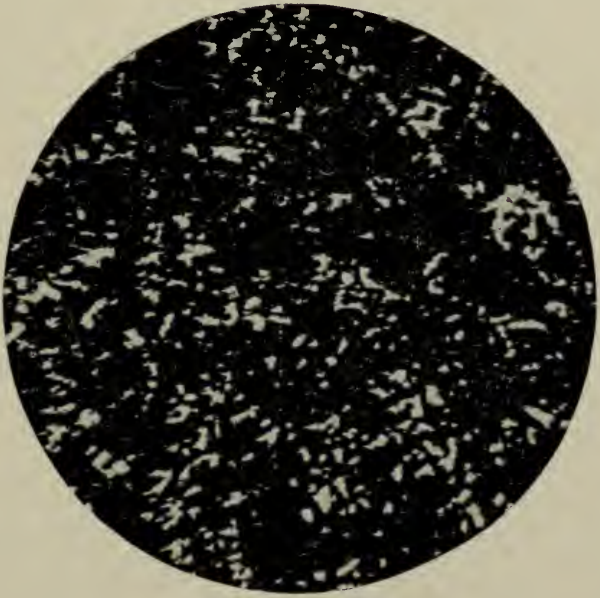

FIG. 9.—Etched Section of Bar No. 10, showing Phosphide Eutectic.

of fine flakes of graphite, small areas of phosphide eutectic in a matrix of ferrite and pearlite. The micrograph, Fig. 6, Plate VIII., which has been taken from bar No. 1, is the typical structure exhibited by these samples, although of course bar No. 6 exhibits a much coarser structure than No. 1.

As the number of the sample increases from No. 7 to No. 10 the structure gets much larger, due to casting temperature, time the metal was allowed to stand in the ladle, &c. The micrograph, Fig. 7, Plate VIII., has been taken from bar No. 10. This shows large flakes of graphite surrounded by areas of ferrite, also in the matrix are observed large areas of phosphide eutectic. These two micrographs are enough to convince anyone that the higher the casting temperature the stronger the resultant casting.

After examination the microsections were deeply etched with a 20 per cent. solution of nitric acid, as suggested by Dr. J. E. Stead, some years ago, to reveal the phosphide eutectic or phosphide of iron as the case may be, and examined under a magnification of 30 diameters.

In a research conducted some years ago by Mr. F. J. Cook and the present author it was observed that strong cast irons, or irons having the highest strength in any one series, exhibited a network structure of the phosphide eutectic or iron phosphide when etched and examined in the above manner, weak irons always showing the phosphide eutectic to be fairly evenly distributed throughout the section.

The micrograph, Fig. 8, Plate IX., is of the bar No. 1, the strongest, hardest, and densest iron of the series, which has also been cast at the highest temperature: a distinct network structure of the phosphide eutectic will be noticed.

The micrograph, Fig. 9, Plate IX., is of bar No. 10, the weakest and softest iron of the series; the phosphide eutectic in this case is evenly distributed throughout the section. This proves that the condition of the phosphide eutectic has a great effect on the strength of cast iron, also that it may be controlled by casting temperature, &c.

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### *Gases evolved on Heating the Specimens for Twelve Hours at a Temperature of 950° C.*

Table VI. gives the amount of gas evolved from the specimens per gramme, also the analysis of the gas.

TABLE VI.

| Sample. | Cubic Centimetres evolved per Gramme | Constituents per Cent. | | |
|---|---|---|---|---|
| | | $CO_2$. | CO. | $H_2N_2$, &c. |
| 1 | 0·402 | 0·98 | 29·62 | 69·40 |
| 2 | 0·362 | 0·99 | 28·46 | 70·55 |
| 3 | 0·310 | 1·21 | 28·25 | 70·54 |
| 4 | 0·261 | 1·36 | 27·89 | 70·75 |
| 5 | 0·206 | 1·61 | 26·46 | 71·93 |
| 6 | 0·172 | 1·82 | 25·05 | 73·13 |
| 7 | 0·126 | 2·32 | 24·76 | 72·92 |
| 8 | 0·101 | 2·58 | 24·02 | 73·40 |
| 9 | 0·085 | 2·96 | 23·78 | 73·26 |
| 10 | 0·056 | 3·21 | 23·03 | 73·76 |

It will be noticed that the lower the temperature of casting the higher the percentage of carbon dioxide, hydrogen, and nitrogen, &c., in the gas evolved, also that the carbon monoxide is decreased. The greatest volume of gas is evolved from sample No. 1 and the least from sample No. 10.

## CONCLUSIONS.

From the results obtained in this investigation the following conclusions are arrived at:

1. A cast iron of a given composition has a certain range of casting temperature to produce a solid, dense, and strong casting free from liquid contraction, which, in the case of the iron under investigation, is between the temperatures of 1428° C. and 1386° C.

2. A cast iron poured at its proper casting temperature will always show a closer microstructure than otherwise, and the phosphide eutectic will be in network formation.

3. The more regular the size of the micro-constituents throughout cast iron, the less liable is the iron to liquid contraction.

4. Blowholes only appear in cast iron when that iron has been poured at a temperature as low or lower than the temperature at which liquid contraction takes place.

5. There is no doubt that the gases play an important part on the soundness of cast iron, as liquid contraction is always more severe in an iron containing a minimum amount of gas held in solution.

# THE OXYGEN CONTENT OF IRON AND STEEL

## AND ITS EFFECT ON THEIR PROPERTIES.[1]

By J. ALLEN PICKARD (London).

The following report is a continuation of previous work on the same subject carried out by the author, and also jointly with Mr. F. M. Potter, and published in *Carnegie Scholarship Memoirs*, 1912, p. 52; and *Journal of the Iron and Steel Institute*, 1914, No. II. p. 181. The results already published refer almost entirely to open-hearth steel, and the present paper deals with other varieties of steel and with cast iron and wrought iron. The results are arranged as follows:—

1. Oxygen Content of Bessemer Steel.
2. „ „ Crucible Steel.
3. „ „ Wrought Iron.
4. „ „ Ingot Iron.
5. „ „ Cast Iron.
6. Evidence of the Influence of Oxygen on the Properties of the Metal.
7. General Conclusions.
8. Summary.

### 1. Bessemer Steel.

The specimens examined were supplied through the courtesy of Messrs. Samuel Fox & Co., Ltd., of Sheffield, and of Mr. C. H. Ridsdale, of Middlesbrough. The specimens were chosen as being representative of their class, and good, average quality material, so that the results may be taken as indicative of the amount of oxygen normally occurring in this

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[1] Report received April 16, 1915.

class of steel. For convenience of reference the samples are arranged in the following tables in ascending carbon order :—

*Acid Bessemer Steel.*

| No. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 1 | 0·42 | 0·61 | 0·066 | 0·049 | 0·057 | 0·014 |
| 2 | 0·45 | 0·85 | 0·080 | 0·056 | 0·048 | 0·017 |
| 3 | 0·49 | 0·90 | 0·098 | 0·048 | 0·054 | 0·014 |
| 4 | 0·51 | 0·83 | 0·048 | 0·046 | 0·056 | 0·018 |
| 5 | 0·53 | 1·07 | 0·060 | 0·045 | 0·050 | 0·007 |
| 6 | 0·75 | 1·01 | 0·082 | 0·049 | 0·049 | 0·014 |
| 7 | 0·80 | 0·85 | 0·090 | 0·046 | 0·059 | 0·006 |

*Basic Bessemer Steel.*

| No. | Carbon. | Silicon. | Sulphur. | Phosphorus. | Manganese. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 8 | 0·01 | Nil. | 0·055 | 0·05 | 0·175 | 0·077 |
| 9 | 0·09 | Nil. | 0·055 | 0·05 | 0·475 | 0·031 |
| 10 | 0·475 | 0·085 | 0·06 | 0·05 | 1·0 | 0·010 |
| 11 | 0·49 | 0·255 | 0·06 | 0·07 | 1·0 | 0·015 |

In looking over the foregoing figures it is possible to notice some correspondence between silicon and oxygen content, but the relation is too ill marked and irregular for much importance to be attached thereto. The very striking exception (No. 11) which has 0·015 oxygen with 0·255 silicon strengthens a suggestion expressed in a former paper that oxygen content is not dependent on the actual percentages of other elements present, but rather on details of procedure in manufacture. Thus it may well be that with a firm making regularly steel of one general composition and observing the same procedure from day to day, the oxygen may be found to vary inversely with the silicon content; while with another maker, steel of approximately the same analysis may contain quite a different amount of oxygen. If this opinion were ultimately substantiated then the oxygen content of the finished metal would appear to be one trustworthy criterion of the excellence of the works practice.

## 2. CRUCIBLE STEEL.

The samples examined were supplied by the kindness of Messrs. Samuel Fox & Co., and of Sir Robert Hadfield. Their analyses and oxygen contents were as follows:—

| No. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Aluminium. | Oxygen. |
|---|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 1 | 0·38 | 0·44 | 4·714 | 0·034 | 0·022 | 1·55 | 0·001 |
| 2 | 1·14 | 0·38 | 0·068 | 0·020 | 0·023 | ... | 0·017 |
| 3 | 1·20 | 0·36 | 0·108 | 0·020 | 0·021 | ... | 0·001 |
| 4 | 1·48 | 0·67 | 0·072 | 0·020 | 0·021 | ... | 0·008 |

## 3. WROUGHT IRON.

Swedish wrought iron, purchased wrought iron of unknown make, and specimens of best Yorkshire iron were examined. The Swedish iron was in the form of a thin flat bar, and drillings were taken along the whole length and gave the following figures:—

| | Per Cent. |
|---|---|
| Carbon | 0·000 |
| Manganese | 0·000 |
| Silicon | 0·000 |
| Sulphur | 0·000 |
| Phosphorus | 0·000 |
| Oxygen | 0·214 |

The purchased iron in the form of plates was drilled at various points in the surface and gave results as under:—

| No. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Oxygen. | Loss. |
|---|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 1 | 0·022 | 0·071 | 0·112 | 0·026 | 0·234 | 0·510 | 0·565 |
| 2 | 0·026 | 0·066 | 0·115 | 0·023 | 0·226 | 0·603 | 0·657 |

The best Yorkshire iron was supplied as a round bar, and the samples for analysis were taken by mounting in the lathe and turning off the end face completely from the circumfer-

## *Errata.*

*Page* 70. The composition of the Swedish iron referred to should read as follows:—

| | Per Cent. |
|---|---|
| Carbon | 0·051 |
| Manganese | 0·019 |
| Silicon | 0·001 |
| Sulphur | 0·012 |
| Phosphorus | 0·065 |
| Oxygen | 0·214 |

*Page* 71. The composition of the best Yorkshire iron should read as follows:—

| | Per Cent. |
|---|---|
| Carbon— | |
| End 1 | 0·122 |
| ,, 2 | 0·110 |
| Manganese— | |
| End 1 | Trace |
| ,, 2 | |
| Silicon— | |
| End 1 | 0·098 |
| ,, 2 | |
| Sulphur— | |
| End 1 | 0·011 |
| ,, 2 | |
| Phosphorus— | |
| End 1 | 0·058 |
| ,, 2 | |
| Oxygen— | |
| End 1 | 0·161 |
| ,, 2 | 0·110 |
| Loss— | |
| End 1 | 0·268 |
| ,, 2 | 0·208 |

ence to the centre and thoroughly mixing the turnings. They gave the following figures :—

| | Per Cent. |
|---|---|
| Carbon— | |
| End 1 | 0·000 |
| ,, 2 | 0·000 |
| Manganese— | |
| End 1 | 0·000 |
| ,, 2 | 0·000 |
| Silicon— | |
| End 1 | 0·000 |
| ,, 2 | 0·000 |
| Sulphur— | |
| End 1 | 0·000 |
| ,, 2 | 0·000 |
| Phosphorus— | |
| End 1 | 0·000 |
| ,, 2 | 0·000 |
| Oxygen— | |
| End 1 | 0·161 |
| ,, 2 | 0·110 |
| Loss— | |
| End 1 | 0·268 |
| ,, 2 | 0·208 |

From these figures it is seen that the Yorkshire iron is lowest in oxygen, the Swedish slightly higher, and the purchased samples very much higher.

An interesting, and at first sight rather puzzling, matter is the difference between the loss in weight of the samples due to abstraction of the oxygen and the total loss in weight, which is especially noticeable in the case of the Yorkshire iron. When a determination of oxygen is made the difference in the weight of the sample before and after treatment is always determined, as a precaution which might serve to detect errors. For instance, if the total loss in weight of the sample were less than the percentage of oxygen found it would be evident that the latter must have been erroneous. In the case of steels it is found in practically every case that the loss in weight, as would be expected, is slightly greater than the percentage of oxygen found, but not very much so. This might readily be explained by loss of moisture from the surface of the drillings in the first operation of the method of analysis, by loss of carbon, of sulphur, and perhaps nitrogen. It had been anticipated that in the case of wrought iron, in which there was no reason to expect that total loss in weight from these causes would be greater than in steel, the oxygen percentage would check fairly well with the loss, but this is not the case. The difference is explainable, however, even with the Yorkshire iron, on the assumption that oxygen is extracted in combination with carbon; and determinations of carbon before and after the oxygen determination were made, with the result that about 80 per cent. of the difference between oxygen percentage and total loss was found to be due to carbon. In both cases the difference between oxygen and loss is nearly the same for samples of the same material, although the oxygen percentage is not so:—

| | Oxygen. | Loss. | Difference. | Carbon, before. | Carbon, after. |
|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| Wrought iron (1) . . . | 0·510 | 0·565 | 0·055 | ... | ... |
| ,, ,, (2) . . . | 0·603 | 0·657 | 0·054 | ... | ... |
| Yorkshire iron (1) . . . | 0·161 | 0·268 | 0·107 | ... | ... |
| ,, ,, (2) . . . | 0·110 | 0·208 | 0·098 | 0·122 | 0·042 |

This result is particularly interesting, since it suggests that oxygen is first eliminated from iron (and presumably also from steel) chiefly in the form of carbon monoxide produced by the initial action of carbon on iron oxide, and that the water formed and weighed only results from the decomposition of this intermediate product, and not directly from the oxide itself. The possibility that all oxygen may be originally present as carbon monoxide is excluded by microscopic evidence adduced by Law,[1] by Matweieff and Steinberg.[2] Law finds that oxide specks were visible under the microscope if the specimen had received a high polish and a magnification of 1000 diameters. When the polished specimen was heated in hydrogen, pits resulted which occupied a greater area than the original spots. The results of Matweieff are corroborative. Steinberg finds that open-hearth steel before deoxidation shows characteristic streaks and cracks in the ferrite crystals. These results show definitely that some oxygen is present as oxides of iron and manganese. Simple decarburisation owing to the heating in hydrogen, irrespective of oxygen in the

[1] *Journal of the Iron and Steel Institute*, 1907, No. II. p. 94.

[2] *Stahl und Eisen*, 1911, vol. xxxi. p. 1062.

metal, is excluded by the fact that decarburisation does not take place to anything like the same degree with steel, which contains more carbon but less oxygen; and also because the decarburisation does not proceed beyond this limit if heating be longer continued.

In passing it may be remarked that this behaviour furnishes corroborative evidence that the objection to the author's method of estimation, based on the assumption that carbon monoxide will not be extracted from steel except in a high vacuum, is quite unfounded. Considerable support is also given to the view, which has gradually been gaining weight, that carbon monoxide, and even dioxide, extracted from steel by heating *in vacuo*, do not exist as such in the steel, but are formed as a result of the action of carbon on oxides present.[1] There is clear evidence that oxygen, originally present as a metallic oxide, parts company with the steel in combination with carbon even when the metal is heated in an atmosphere of hydrogen.

## 4. "INGOT" IRON.

A sample of this material supplied from America "guaranteed 99·86 per cent. iron" with the following analysis:—

| | Per Cent. |
|---|---|
| Carbon | 0·040 |
| Manganese | 0·040 |
| Silicon | nil |
| Sulphur | 0·020 |
| Phosphorus | 0·004 |
| Aluminium and oxygen | nil |
| Copper | nil |
| Hydrogen | 0·001 |
| Oxygen | 0·009 |
| Nitrogen | 0·004 |

was found by the author to contain $O = 0·092$ per cent.

Dr. Stead has kindly informed the author that for another ingot iron he has obtained the following figures:—

| | Oxygen per Cent. |
|---|---|
| Before deoxidation | 0·07 |
| After deoxidation | 0·02 |

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[1] See the author's paper, "The Relation of Oxygen to other Gases in Steel," read before the Sheffield Society of Engineers and Metallurgists, March 1915.

A specimen of iron which had remained under a highly oxidising slag for many hours in a basic open-hearth furnace was kindly sent to the author by Mr. W. J. Brooke, of the Shelton Iron, Steel and Coal Co. In this case all impurities had been practically eliminated by the strong oxidation, and assuming that sufficient time had been allowed for the oxide added to dissolve to saturation in the bath, and for the excess to float up and enter the slag, the metal probably contained as much oxide as it could hold without the presence of suspended globules of oxide. The sample, on analysis, yielded:—

| | Per Cent. |
|---|---|
| Carbon . . . . . . . . | 0·022 |
| Manganese . . . . . . . | 0·034 |
| Sulphur . . . . . . . . | 0·038 |
| Phosphorus . . . . . . . | 0·008 |
| Oxygen . . . . . . . . | 0·092 |

If it be assumed that in this case the bath was saturated with oxide and contained no oxide in suspension, then, calculating oxygen as FeO, the figure 0·405 per cent. FeO is obtained for the solubility of oxide of iron in liquid metal. In this place it may be interesting to recall the blown Bessemer metal (No. 8, p. 69) which contained 0·077 per cent. of oxygen and was probably not completely saturated.

The foregoing figures for ingot iron may be considered definitely to prove that oxide of iron is soluble to a moderate extent in liquid iron, and permit of an approximate estimate of the extent of this solubility being made. They cannot, however, be taken to show that the oxide remains dissolved when the steel solidifies, although the microscopical evidence already cited permits the belief that a considerable part also remains in solid solution.

## 5. Cast Iron.

Some attention having been drawn to a paper by Mr. J. E. Johnson, jun.,[1] claiming the most remarkably beneficial results from the presence of oxygen in cast iron, some specimens of grey and of white irons were examined.

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[1] *Transactions of the American Institute of Mining Engineers*, 1914, vol. xlvii. p. 453.

When the exceedingly complex nature of iron is borne in mind, and the very considerable percentage of carbon, silicon, and manganese often present, it seems *prima facie* extremely unlikely that oxygen can coexist therein, and it was consequently with considerable surprise that unmistakable indications of its presence in white iron were found. Two specimens of chilled iron were kindly supplied by Mr. W. M. Frank Schneider, of the British Griffin Chilled Iron and Steel Co. Specimen No. 1 was stated to be of excellent quality for the special purposes of the makers, and No. 2 not quite so good. The analyses of the two samples were as follows:—

| | (1) | (2) |
|---|---|---|
| Combined carbon . | 2·656 per cent. | 0·797 per cent. |
| Graphite . . . | 0·550 ,, | 2·450 ,, |
| Silicon . . . | 0·615 ,, | 0·699 ,, |
| Sulphur . . . | 0·067 ,, | 0·126 ,, |
| Phosphorus . . | 0·198 ,, | 0·207 ,, |
| Manganese . . . | 0·987 ,, | 0·532 ,, |
| Oxygen . . . | 0·017 ,, | 0·021 ,, |

This material being particularly hard and tough, and consequently difficult to disintegrate, it may not be out of place to state here that the samples for analysis were obtained by drilling with a specially tempered flat drill. The outside of the samples was carefully cleaned on an emery wheel and the outer skin drilled well through before any material was collected for analysis. The samples never became more than warm to the touch during drilling, and closely agreeing results for oxygen were obtained on 30 gramme samples.

From the above figures it is impossible to doubt that small amounts of oxygen occur in white iron. What the state of combination may be, and what effect, if any, its presence may have on the quality of the metal it is impossible to state. Taken in conjunction with the fact that no sample of grey iron examined by the author, or by other investigators, except Johnson's special irons, has been found to contain oxygen even up to 0·01 per cent., it is reasonable to conclude that the rapid chilling has the effect of locking up carbon monoxide which would otherwise escape. It is obvious that the slight difference in oxygen percentage is incapable of explaining the difference between the quality of these two specimens—indeed the difference between the respective percentages in the two samples of the other constituents is incomparably more significant. The chief interest attaching to the results is that they show that oxygen is present in material from which it has hitherto usually been assumed to be absent; and that an amount of oxygen which would be important if found in steel may exist in material containing even such, comparatively, large amounts of silicon, carbon, and manganese, as commercial cast irons.

The influence of oxygen on the properties of steel has so far been chiefly a matter of conjecture. Cushman [1] and also Law [2] consider that oxygen has a marked effect in increasing the corrosion of the metal through rusting. Law found that plates of ordinary steel were corroded in London atmosphere at a rate 24 per cent. greater than were plates of similar steel deoxidised by adding fair amounts of ferro-silicon.

Campbell [3] states that since the ductility of open-hearth steel increases as the composition of pure iron is approached, oxygen cannot have a very great deleterious effect, since it will be high in the purer and more ductile irons. He even speculates (p. 524) that oxide of iron may confer abnormal adhesive power. Bradley Stoughton, on the other hand, takes an opposite view. In his "Metallurgy of Iron and Steel," 1908, pp. 173–6, he states, "Oxygen occurs in iron and steel as FeO and $Fe_2O_3$. In either form its presence is very harmful, producing brittleness in both hot and cold steel, besides causing liability to blowholes. . . . There is probably no constituent more harmful to steel than oxygen . . . the effect of oxygen is somewhat similar to that of sulphur, and, in common parlance, makes the steel 'rotten.'"

It is evident from these opinions that the effect of oxygen on steel is a matter of dispute, and while endeavouring to keep an open mind on the subject we may consider here a few examples of materials which have proved unsatisfactory in use, for whose failure no obvious reason offered itself except the presence of oxygen.

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[1] *Proceedings of the American Society for Testing Materials*, 1911, vol. xi. p. 399.

[2] *Journal of the Institute of Metals*, 1912, No. 2, pp. 222–230.

[3] "Manufacture and Properties of Iron and Steel," p. 480.

## 6. EVIDENCE OF THE INFLUENCE OF OXYGEN ON THE PROPERTIES OF THE METAL.

In some cases it has been possible to obtain specimens of satisfactory material similar to those which have failed, and when these have been found to contain less oxygen than the unsatisfactory material there is ground for supposing oxygen to be connected with the cause of failure. In many cases, however, no noteworthy difference could be found between oxygen percentages in good and bad material, and accordingly these failures could not be taken as evidence of the harmful effects of oxygen, and have not been included here.

A specimen of steel which had given rise to "non-sizing" in wire-drawing, together with another steel practically identical in composition but perfectly satisfactory in this respect, was referred to the author with the following results:—

| | Oxygen per Cent. |
|---|---|
| "Non-sizing" specimen | 0·021 |
| Normal specimen | 0·012 |

Analysis and numerous mechanical tests of a searching character had been carried out on the specimens before the determination of oxygen, but had failed to bring to light any difference to which the defect could reasonably be attributed.

In several machines in which a certain part was subjected to jarring, strain, and occasional rapid and irregular alterations of stress, one of these parts fractured unexpectedly. The material from which it was manufactured had the following analysis:—

| | Per Cent. |
|---|---|
| Carbon | 0·35 |
| Manganese | 0·64 |
| Silicon | 0·29 |
| Sulphur | 0·035 |
| Phosphorus | 0·035 |
| Nitrogen | 3·3 |

and the fractured part agreed almost exactly in composition with similar members which did not break. On carrying out estimations of oxygen in the broken piece, and also in the satisfactory material, the following results were found:—

| | Oxygen per Cent. |
|---|---|
| Broken part | 0·022 |
| Satisfactory part | 0·008 |

The figures suggest strongly that oxygen was to blame in this case.

The author was favoured by the North-East Coast Institution of Engineers and Shipbuilders with a specimen from a consignment of ship plates which had failed mysteriously.[1] On analysis the specimen gave the following figures:—

| | Per Cent. |
|---|---|
| Graphite | trace |
| Combined carbon | 0·06 |
| Manganese | 0·611 |
| Silicon | 0·008 |
| Sulphur | 0·108 |
| Phosphorus | 0·091 |
| Arsenic | trace |
| Oxygen | 0·035 |

Unfortunately a comparison specimen of good material was not available. In the author's opinion the oxygen percentage is dangerously high and likely to produce bad effects, but in view of the rest of the analysis, particularly as regards sulphur and phosphorus, it would be unwise to attribute the failure to this cause alone.

The analysis of another sample of ship plate, kindly sent by Mr. S. A. Houghton, which failed unaccountably, has already been published,[2] but it may not be out of place to refer to it again here. In this case the general analysis was much better and the oxygen lower:—

| | Carbon. | Silicon. | Manganese. | Sulphur. | Phosphorus. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| Outside | 0·225 | 0·082 | 0·598 | 0·04 | 0·054 | 0·017 |
| Inside | 0·22 | 0·094 | 0·594 | 0·039 | 0·052 | |

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[1] For a full account of this case, and discussion, see *Transactions of the North-East Coast Institution of Engineers and Shipbuilders*, November 1914.

[2] *Journal of the Iron and Steel Institute*, 1914, No. I. p. 308.

Here again, since it is evident from the many results given that oxygen need not exceed 0·01 per cent. in first quality material, this element is at least suspect.

A specimen of acid open-hearth steel which was required to withstand very heavy sudden blows soon after putting into service broke suddenly into a number of pieces. Analysis showed:—

| | Per Cent. |
|---|---|
| Carbon | 0·45 |
| Silicon | 0·20 |
| Manganese | 0·77 |
| Sulphur | 0·032 |
| Phosphorus | 0·038 |
| Oxygen | 0·050 |

The oxygen is seen to be exceedingly high for this class of material, while the remainder of the analysis is irreproachable. Microscopic examination failed to detect any error in heat treatment. The conclusion that oxygen was accountable for this failure seems therefore justified.

## 7. General Conclusions.

For convenience in reference the majority of the analytical data so far collected are given in the following tables:—

*Acid Bessemer.*

| No. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 1 | 0·42 | 0·61 | 0·066 | 0·049 | 0·057 | 0·014 |
| 2 | 0·45 | 0·85 | 0·080 | 0·056 | 0·048 | 0·017 |
| 3 | 0·49 | 0·90 | 0·098 | 0·048 | 0·054 | 0·014 |
| 4 | 0·51 | 0·83 | 0·048 | 0·046 | 0·056 | 0·018 |
| 5 | 0·53 | 1·07 | 0·060 | 0·045 | 0·050 | 0·007 |
| 6 | 0·75 | 1·01 | 0·082 | 0·049 | 0·049 | 0·014 |
| 7 | 0·80 | 0·85 | 0·090 | 0·046 | 0·050 | 0·006 |
| | | | | | Mean . . . | 0·013 |
| | | | *Basic Bessemer.* | | | |
| 8 | 0·01 | 0·175 | nil | 0·055 | 0·05 | 0·077 |
| 9 | 0·09 | 0·475 | nil | 0·055 | 0·05 | 0·031 |
| 10 | 0·475 | 1·0 | 0·085 | 0·06 | 0·05 | 0·010 |
| 11 | 0·49 | 1·0 | 0·255 | 0·06 | 0·07 | 0·015 |
| | | | | | Mean . . . | 0·019[1] |

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[1] Omitting No. 8, which was not deoxidised

## *Acid Open-Hearth.*

| No. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 12 | 0·67 | 0·73 | 0·95 | 0·035 | 0·027 | 0·004 |
| 13 | 0·79 | 0·65 | 0·21 | 0·030 | 0·050 | 0·021 |
| 14 | 0·93 | 0·68 | 0·035 | 0·031 | 0·027 | 0·007 |
| 15 | 1·08 | 0·62 | 0·024 | 0·033 | 0·022 | 0·014 |
| 16 | 1·18 | 0·65 | 0·056 | 0·027 | 0·025 | 0·006 |
| 17 | 1·33 | 0·42 | 0·140 | 0·030 | 0·024 | 0·004 |
| 18 | 1·55 | 0·49 | 0·100 | 0·027 | 0·026 | 0·011 |
| | | | | | Mean . . . | 0·010 |
| *Basic Open-Hearth.* | | | | | | |
| 19 | 0·10 | ... | 0·05 | ... | ... | 0·037 |
| 20 | 0·14 | 0·35 | 0·020 | 0·033 | 0·018 | 0·011 |
| 21 | 0·20 | ... | 0·04 | ... | ... | 0·030 |
| 22 | 0·23 | 0·70 | 0·1–·15 | 0·060 | 0·026 | 0·014 |
| 23 | 0·26 | 0·49 | 0·120 | 0·030 | 0·031 | 0·005 |
| 24 | 0·30 | ... | 0·05 | ... | ... | 0·029 |
| 25 | 0·32 | 0·62 | 0·1–·15 | 0·051 | 0·020 | 0·041 |
| 26 | 0·33 | 0·62 | 0·1–·15 | 0·057 | 0·025 | 0·023 |
| 27 | 0·35 | 0·56 | 0·182 | 0·027 | 0·020 | 0·007 |
| 28 | 0·41 | 0·52 | 0·026 | 0·032 | 0·023 | 0·017 |
| 29 | 0·44 | ... | 0·04 | ... | ... | 0·027 |
| 30 | 0·54 | 0·69 | 0·085 | 0·022 | 0·024 | 0·003 |
| 31 | 0·55 | 0·97 | 0·1–·15 | 0·055 | 0·011 | 0·017 |
| 32 | 0·55 | ... | 0·05 | ... | ... | 0·020 |
| 33 | 0·61 | 0·74 | 0·1–·15 | 0·053 | 0·021 | 0·041 |
| 34 | 0·66 | 0·65 | 0·100 | 0·033 | 0·052 | 0·006 |
| 35 | 0·75 | 0·38 | 0·025 | 0·025 | 0·022 | 0·026 |
| 36 | 0·82 | 0·67 | 0·096 | 0·030 | 0·028 | 0·006 |
| 37 | 1·00 | 0·67 | 0·036 | 0·016 | 0·025 | 0·007 |
| | | | | | Mean . . . | 0·019 |

## *Crucible Steel.*

| No. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Oxygen. | Aluminium. |
|---|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent | Per Cent. |
| 38 | 0·38 | 0·44 | 4·71 | 0·034 | 0·022 | 0·001 | 1·55 |
| 39 | 1·14 | 0·38 | 0·068 | 0·020 | 0·023 | 0·017 | ... |
| 40 | 1·20 | 0·36 | 0·108 | 0·020 | 0·021 | 0·001 | ... |
| 41 | 1·48 | 0·67 | 0·072 | 0·020 | 0·021 | 0·008 | ... |

*Wrought Iron.*

| | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| Swedish . . | 0·05 | 0·07 | 0·02 | 0·01 | 0·02 | 0·214 |
| Unknown . . | 0·022 | 0·071 | 0·112 | 0·026 | 0·234 | 0·510 |
| ,, . . | 0·026 | 0·066 | 0·115 | 0·023 | 0·226 | 0·603 |
| Best Yorkshire . | 0·122 | 0·02 | 0·05 | 0·010 | 0·05 | 0·136 |

*Ingot Iron.*

| | Carbon. | Manganese. | Silicon. | Sulphur | Phosphorus. | Oxygen. |
|---|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| American . . . | 0·040 | 0·040 | nil | 0·020 | 0·004 | 0·092 |
| English— | | | | | | |
| Before deoxidation . . . | ... | ... | ... | ... | ... | 0·092 |
| Before deoxidation (Dr. Stead) | ... | ... | ... | ... | ... | 0·07 |
| After deoxidation (Dr. Stead) | ... | ... | ... | ... | ... | 0·02 |

## SUMMARY.

*Solubility of Ferrous Oxide in Iron.*—The results in section 4 indicate 0·405 per cent. FeO for the solubility of ferrous oxide in liquid steel nearly free from other elements.

*The Effect of Oxygen on the Properties of the Metal.*—The results obtained all point in one direction—that oxygen in steel, if exceeding 0·01 per cent., tends to produce brittleness under shock. The problem is one of unusual difficulty since the straightforward method of making a direct comparison between steels similar in every respect except oxygen content, and mechanically and microscopically testing them to discover in what respects they differ, is practically impossible. The only method available appears to be to test actual failures and compare them with normal material of the same class, the solution of the problem being consequently a slow matter.

Against the above conclusion it may be urged that many wrought irons and "ingot" irons are not at all brittle under shock. But here it must be borne in mind that the practical absence of carbon from these materials produces a profound difference in character, and it is very likely that the effect of oxygen on nearly pure iron will differ from its effect on steel.

# THE HEAT BALANCE OF A BLAST-FURNACE STOVE.[1]

By R. S. G. KNIGHT, B.Sc. (London).

The work recorded in this report was carried out at the blast-furnace plant of The Skinningrove Iron Company Limited, Skinningrove, Yorkshire. Unfortunately, owing to the disposition of the plant, which did not permit of a direct measurement of the gas supplied to the stove being made, it was not possible to obtain as complete data for a heat balance as was hoped for. Nevertheless, by assuming a certain reasonable radiation loss, and averaging the results of the analyses of the products of combustion, it is possible to deduce from the experimental figures an approximate heat balance.

## General Description of the Plant.

The stove selected for these experiments was one of a battery of thirteen Cowper stoves used for driving five furnaces. At the time of this investigation, however, three stoves and one furnace were down for repairs, so that the four furnaces were being driven from ten stoves.

The stoves draw their gas from a common underground main into which the whole of the gas from the furnaces is led, the surplus gas being used on other parts of the plant. The hot blast from the batch of stoves is led into a common main running along the back of the furnaces and communicating with each of these by the horse-shoe main. In practice the stoves are worked as a whole, there being no rigorous division between them for any furnace. Of the ten stoves in use for the four furnaces, six are on gas and four on blast at the same time, each furnace being blown from one stove. The stove is usually kept on gas for about one and a half hours, and on

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[1] Received June 10, 1915.

blast for one hour, but these times vary with the working of the furnaces and the condition of the stoves. As a general rule each stove blows for half an hour on one furnace and for the remaining half hour on another furnace, so that No. 11 stove usually blew No. 5 furnace during the first half hour and was then changed over to No. 4 furnace, a fresh stove taking its place on No. 5. The whole working of the stoves, however, has to be run according to the requirements of the furnaces, so that no hard and fast rules can in any way be laid down.

## DESCRIPTION OF THE STOVE (No. 11) USED FOR THE TRIAL.

The stove is shown in sectional plan and elevation in Figs. 1A and 1B, except that the flame flue, instead of being circular as there shown, is elliptical. The stove is 60 feet 6 inches high and 23 feet diameter, and is lined with firebrick to a

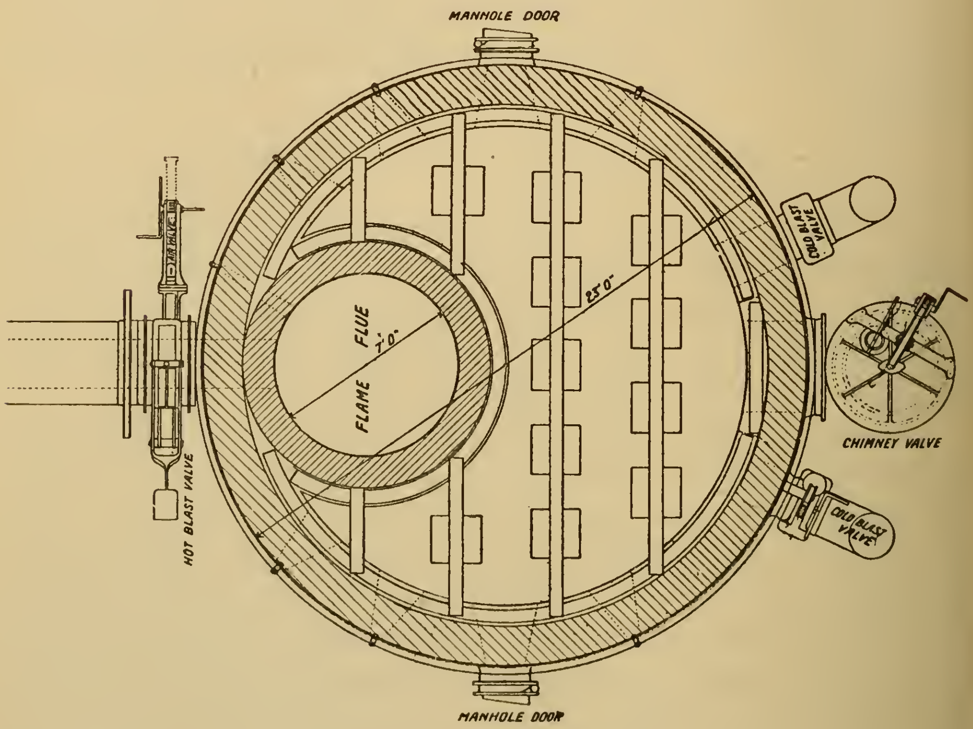

MANHOLE DOOR
AIR VALVE
FLUE
7' 0"
FLAME
25' 0"
COLD BLAST VALVE
CHIMNEY VALVE
COLD BLAST VALVE
HOT BLAST VALVE
MANHOLE DOOR

FIG. 1A.—Sectional Plan of Stove.

depth of 1 foot 6 inches in the regenerator portion and 2 feet 8 inches in the flame flue.

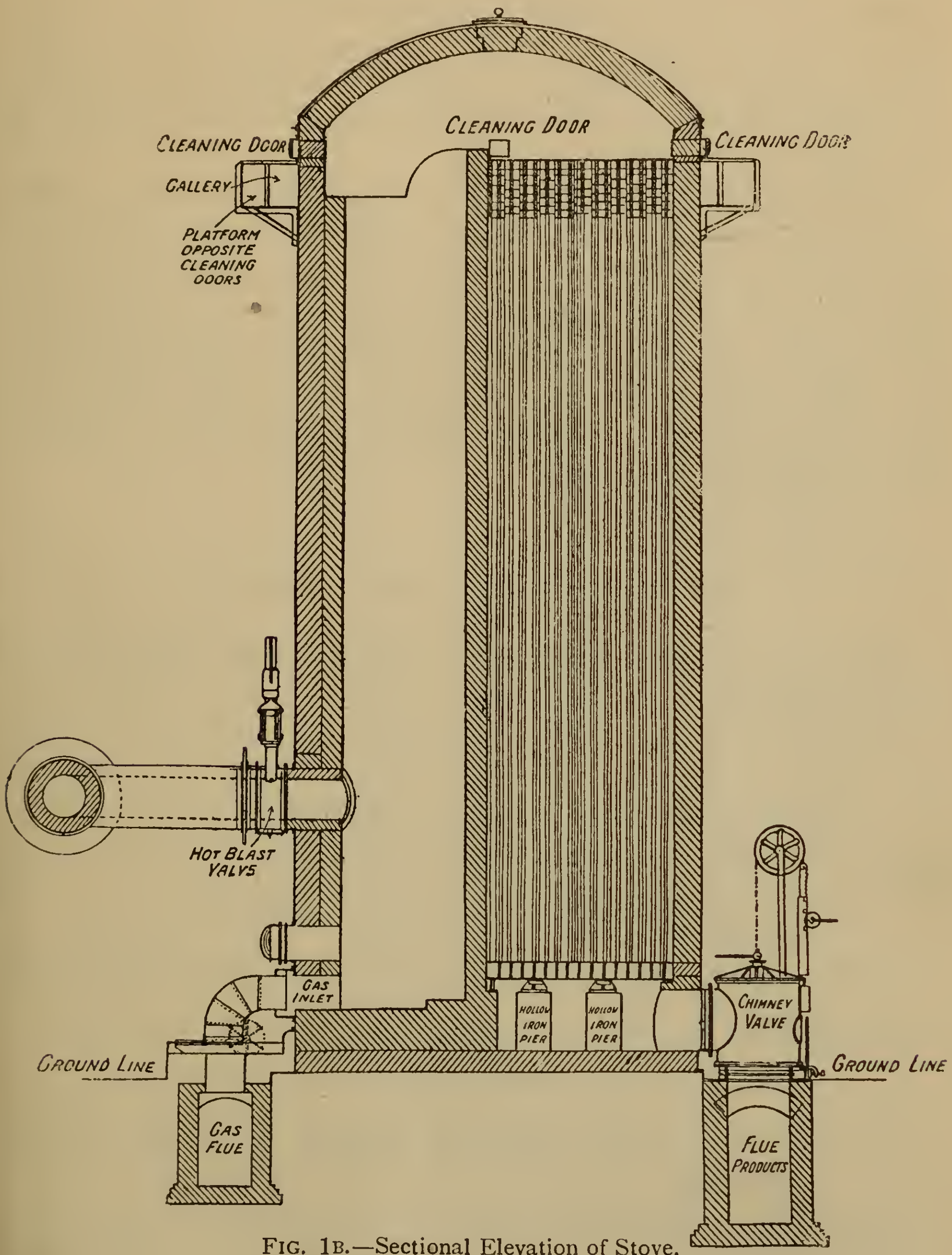

CLEANING DOOR
CLEANING DOOR
CLEANING DOOR
GALLERY
PLATFORM OPPOSITE CLEANING DOORS
HOT BLAST VALVE
GAS INLET
HOLLOW IRON PIER
HOLLOW IRON PIER
CHIMNEY VALVE
GROUND LINE
GROUND LINE
GAS FLUE
FLUE PRODUCTS

FIG. 1B.—Sectional Elevation of Stove.

The gas enters the stove from the underground main through the gas nozzle at the bottom of the flame flue, the supply being regulated by a plate valve at the base of the nozzle. The air for combustion is drawn from the atmosphere through the air port situated about 7 feet from the ground and a little to the left of the gas inlet. The products of combustion travel to the top of the flame flue and then pass down the regenerator portion, composed of firebrick chequer work, through the valve box into the flue leading to the stack.

On the reversal the air enters from the cold blast main through two smaller mains (each 21 inches diameter), one on each side of the valve box. The air travels in the reverse direction to that previously taken by the gas, passing first through the regenerator and then down the flame flue to the hot blast main, which is situated 14 feet 6 inches from the ground level and immediately above the air port. The hot blast valve is water cooled.

## THE HEAT BALANCE OF A STOVE.

The several items comprising the balance-sheet may be set out as follows:—

*Debit Side.*

1. The heat produced by the combustion of the gas.
2. The sensible heat contained in the gas.
3. The heat contained in the dust entering the stove with the gas.
4. The heat contained in the moisture entering the stove with the gas.

*Credit Side.*

1. The heat carried away as sensible heat in the flue products.
2. The heat required to raise the temperature of the blast.
3. The heat used in raising the temperature of the moisture contained in the blast to the hot blast temperature.
4. The heat carried off by the dust swept from the stove into the flue.

5. The heat carried off by the water vapour leaving the stove.
6. The heat lost from the stove by radiation, conduction, and convection.

The above balance is valid only when the condition of the stove is the same at the end of the trial as at the commencement. During the period the stove is on gas the chequer work is heated up to a certain extent. The flue temperature, as may be seen from Fig. 2, becomes nearly constant after about half an hour. This shows that the larger the amount of gas put into the stove the greater is the amount of chequer work raised up to the average temperature, that is, the greater is the heat reserve of the stove. In a single reversal it is quite possible to get more heat out of the stove than was put in during the period the stove was on gas. Therefore, in order to obtain a reliable heat balance, it is absolutely necessary to carry the test over as many consecutive reversals as possible, the longer the trial the greater, *ceteris paribus*, being the accuracy.

In this investigation the test was run for a period of about twenty-four hours, comprising nine complete reversals. The methods and apparatus used in the evaluation of the several items of the balance-sheet to which special attention was given will now be described in detail.

## 1. THE HEAT PRODUCED BY THE COMBUSTION OF THE GAS.

The determination of this factor involved the following:—

(*a*) The temperature and pressure of the gas.
(*b*) The calorific value of the gas.
(*c*) The amount of gas at N.T.P. entering the stove.

(*a*) The temperature of the gas was taken by a Hoskins base metal couple and indicator supplied by the Foster Instrument Co., and previously calibrated in the Fuel laboratories of the Imperial College of Science, London. A rivet was removed from the gas nozzle near the plate valve and the couple fixed in at this point. In this position the effect of direct radiation from the wall of the flame flue was less than it would have been had the couple been inserted on the side of the bend near the gas inlet. A pressure gauge was fixed near the mouth of the nozzle through a similar rivet hole. Fig. 2 shows the records of both the gas and flue temperatures obtained in experiments 1 and 7 of the test.

(*b*) The calorific value of the blast-furnace gas was obtained by calculation from its analysis. Since the gas varies but little in its composition three samples only were taken, and these at equal intervals during the trial. Each sample was continuous over the period the stove was on gas, and was drawn from the nozzle into a gas holder over glycerine and water (1 : 1) and analysed at the completion of the test.

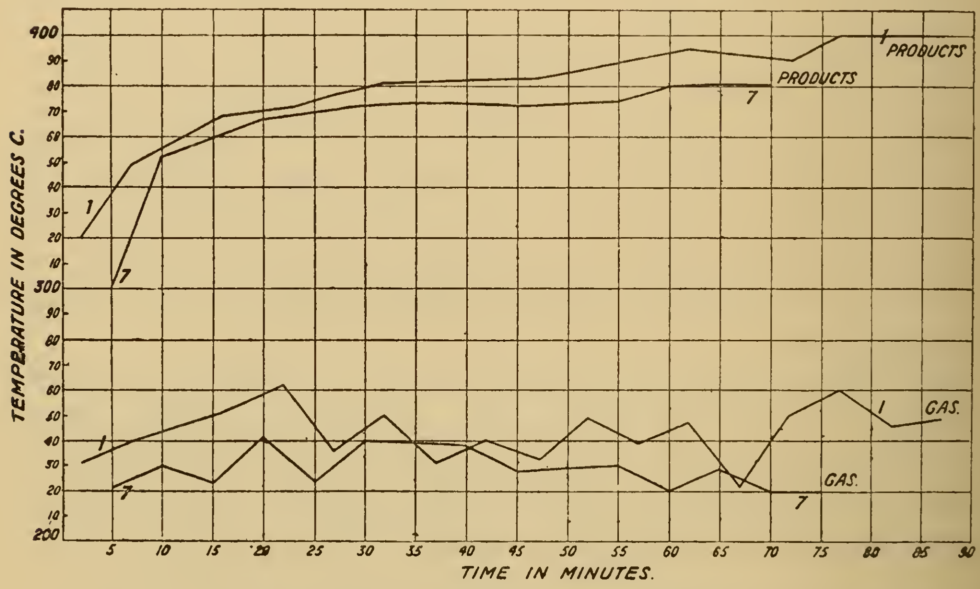


FIG. 2.—Records of Gas and Flue Temperatures.

(*c*) The measurement of the amount of gas entering the stove involves the determination of its velocity, but after many attempts it was found impossible to obtain this directly. The method tried was to fix specially designed Pitot tubes in the mouth of the nozzle, connect these to a recording differential pressure gauge, and from the average dynamic pressure to calculate the velocity.

The Pitot tubes were bound securely in position and the space between the nozzle and the opening in the stove was closed up with clay to prevent the entrance of air, which would produce eddy currents and so vitiate the records. The differential recorder used in conjunction with the tubes was of the type shown in Fig. 4, but having a range of only half an inch pressure of water. The records thus obtained were altogether unsatisfactory, showing a velocity head of very much less magnitude than was reasonable, and corresponding in no way with the variations of the gas pressure. Careful search showed that the cause of failure was due to the fact that the gas entered the stove with an eddying motion almost at right angles to the direction of flow. In those stoves where a portion of the air for combustion is drawn through an inner tube fixed in the gas nozzle, this eddying motion can be readily seen, as the flame is quite black in the centre but increases in luminosity towards the circumference, the dust having been thrown outwards by the circular movement. In No. 11 stove the eddy was indicated by the stream lines on the dust in the mouth of the nozzle, which lay parallel to one another in a direction about 70° from that of the gas flow.

The eddying motion is undoubtedly due to the change of pressure occurring at the plate valve, caused by the rush of gas through a restricted opening. The pressure on the furnace side of the plate valve was approximately 3 inches water gauge, whilst in the nozzle the gas was under a suction of about $1\frac{1}{2}$ inches water gauge.

It will be seen from the drawing of the stove shown in Figs. 1A and 1B that, under existing conditions, at no point between the mouth of the nozzle and the underground gas main could any reasonable measurement of the velocity be made except by fully opening the plate valve and fixing an adjustable diaphragm at the mouth of the nozzle. Even in this case the measurement would have had to be taken as far as possible from the diaphragm, as the effect of the reversal of pressure would be apparent for some distance on the furnace side of the diaphragm.

The amount of gas passing into the stove might be determined indirectly either from the quantity of flue products or from the amount of air used for combustion. Both these methods were impossible on account of the disposition of the plant.

### 2. The Sensible Heat in the Gas entering the Stove.

The experimental data required for the calculation of this item, namely, the measurement of the temperature, pressure, and quantity of gas used in each test, have already been considered in the previous paragraph.

### 3. The Heat carried off in the Flue Products.

The evaluation of this factor requires a knowledge of the temperature of the products of combustion, together with the average analysis and quantity passing into the flue during each period the stove is on gas.

The temperature was taken by a base metal thermo-couple inserted in the short length of main between the stove and the valve box, and connected to an indicator from which readings were taken at five minute intervals. During each run a continuous sample of the products was drawn into a gasholder containing glycerine and slightly acid water (1 : 1), from a tube fixed in the valve box. These samples were analysed at the completion of the test.

The determination of the quantity of products and of the excess air used in the combustion is best found by calculation from the amount of gas used, on the basis of the carbon content of the gas and of the products. Since, however, the amount of gas used could not be directly measured, it is impossible to get either the quantity of products or the amount of excess air by direct methods.

### 4. The Heat required to raise the Temperature of the Blast.

In order to find the heat taken up by the blast it is necessary to determine the temperature and pressure of the cold blast, the temperature of the hot blast, and the quantity of blast blown per hour.

The temperature of the cold blast was read at intervals from a mercury thermometer placed in one of the two inlet mains. The blast pressure was taken from a Bristol recording gauge permanently connected up to the cold blast main.

The hot blast temperature was taken by a base metal couple fixed in the hot blast main directly behind the stove valve, and connected up to a calibrated recorder from which readings were taken at intervals of five minutes.

The quantity of blast used was calculated from its velocity in each of the two inlet mains. For this purpose Pitot tubes of the form shown in Fig. 3 were employed. These tubes were fixed in each of the mains with the tips facing the air steam, the dynamic tip being about one-sixth of the diameter of the main from the circumference. The two tubes were connected up to the differential pressure recorder (Fig. 4), which consists of a float moving in water contained in a closed cylindrical iron vessel. The static pressure acts on the upper side of the float and the combined static and dynamic pressures act on the under side, so that the movement of the float is caused by the difference between these, namely, the dynamic pressure of the air. This difference is recorded by a pen attached to the float marking on the chart affixed to the revolving drum. The instrument was designed to work at 5 lbs. pressure and to have a range of $1\frac{1}{2}$ inches with a magnification of 4 : 1. The two records shown in Fig. 5 were taken

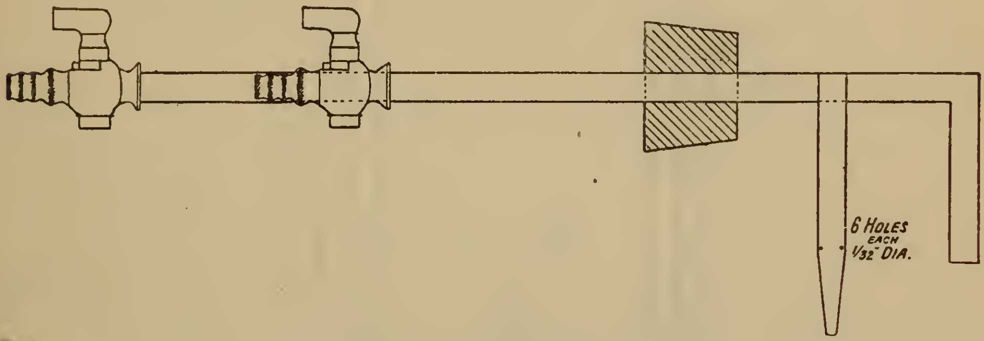


FIG. 3.—Pitot Tubes.

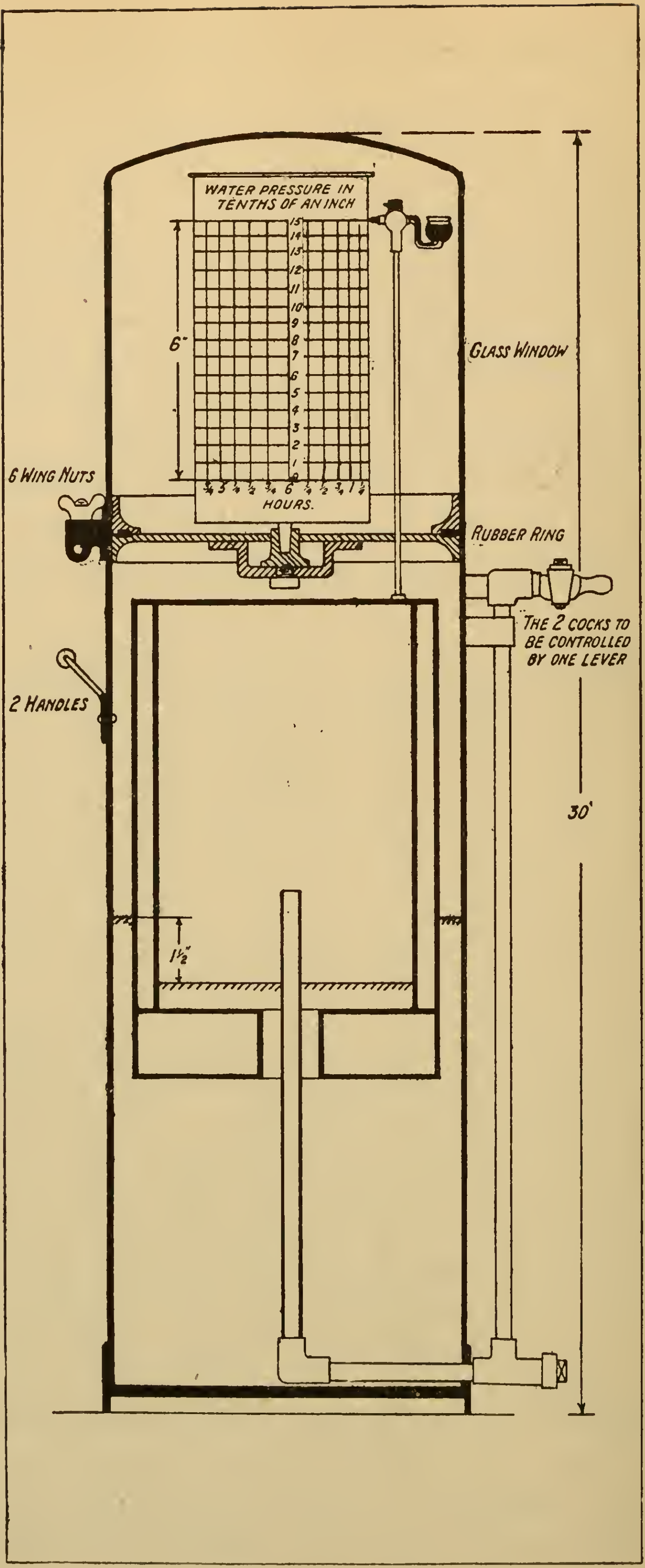

WATER PRESSURE IN TENTHS OF AN INCH
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
6"
¾ 5 ¼ ½ ¾ 6 ¼ ½ ¾ 1 ¼
HOURS.
6 WING NUTS
GLASS WINDOW
RUBBER RING
THE 2 COCKS TO BE CONTROLLED BY ONE LEVER
2 HANDLES
30'
1½"

FIG. 4.—Differential Pressure Recorder.

during the same test, the one from the right-hand main and the other from the left-hand main.

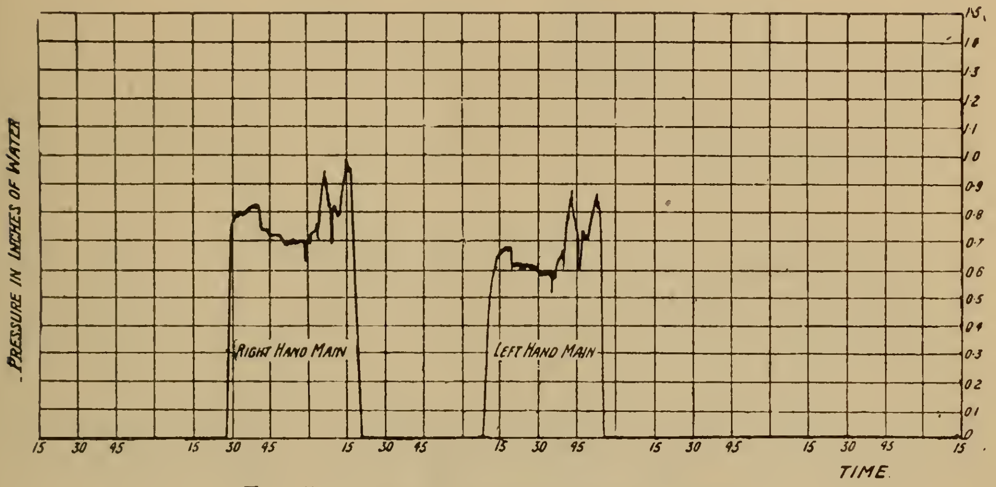


FIG. 5.—Dynamic Pressure Records of Blast.

The velocity of the blast is calculated from the average dynamic pressure during the test, using Griggs's formula.[1]

$$V = 0{\cdot}997\sqrt{\frac{2ghw}{12d}}$$

where

V = The velocity in ft./sec. at the temperature and pressure of the main.
$g$ = Acceleration due to gravity (32·2 ft./sec.).
$w$ = The weight of 1 cubic foot of water = 62·4 lbs.
$h$ = The dynamic pressure in inches water gauge.
$d$ = The weight of 1 cubic foot of the gas at the temperature and pressure of the main.

## DETAILS OF THE TRIAL.

The trial was commenced at 11.53 A.M. on the 11th March 1915, when the stove was put on gas, and was continued during nine reversals ending at 11.48 A.M. on the 12th March.

A summary of the results obtained is given in the two following tables.

---

[1] Griggs, *Journal of Gaslighting*, Nov. 1912.

TABLE I.—*Stove on Gas.*

| No. of Experiment. | Time. | | Average Gas Temp. | Average Flue Temp. | Average Gas Pressure in Ins. w.g. | Gas Plate Opening. Inches. | Air Port Opening. Inches. | Analysis of Gas. | Analysis of Products. |
|---|---|---|---|---|---|---|---|---|---|
| | H. | M. | | | | | | | |
| 1 | 1 | 31 | 243 | 380 | −1·4 | $17\frac{1}{4}$ | $6\frac{3}{8}$ | $CO_2$ 9·2<br>CO 30·5<br>$H_2$ 1·3<br>$N_2$ 59·0 | $CO_2$ 12·2<br>$O_2$ 9·8<br>$N_2$ 78·0 |
| 2 | 1 | 28 | 249 | 371 | −1·3 | $18\frac{1}{2}$ | 7 | ... | $CO_2$ 11·2<br>$O_2$ 12·2<br>$N_2$ 76·6 |
| 3 | 1 | 19 | 256 | 369 | −1·5 | $17\frac{7}{8}$ | $6\frac{5}{8}$ | ... | $CO_2$ 14·9<br>$O_2$ 7·6<br>$N_2$ 77·5 |
| 4 | 1 | 19 | 266 | 373 | −1·3 | $18\frac{5}{8}$ | $6\frac{7}{8}$ | $CO_2$ 9·7<br>CO 29·5<br>$H_2$ 0·7<br>$N_2$ 59 1 | $CO_2$ 15·3<br>$O_2$ 7·7<br>$N_2$ 77·0 |
| 5 | 1 | 54 | 246 | 356 | −1·4 | $17\frac{3}{4}$ | $5\frac{1}{8}$ | ... | $CO_2$ 17·2<br>$O_2$ 5·4<br>$N_2$ 77·4 |
| 6 | 1 | 34 | 228 | 374 | −1·5 | $17\frac{1}{2}$ | $6\frac{1}{4}$ | ... | $CO_2$ 15·9<br>$O_2$ 5·9<br>$N_2$ 78·2 |
| 7 | 1 | 18 | 229 | 367 | −1·4 | $17\frac{5}{8}$ | $5\frac{3}{4}$ | $CO_2$ 9·5<br>CO 30·0<br>$H_2$ 1·2<br>$N_2$ 59·3 | $CO_2$ 18·4<br>$O_2$ 4·7<br>$N_2$ 76·9 |
| 8 | 1 | 23 | 222 | 356 | −1·2 | (*a*) $18\frac{1}{8}$<br>(*b*) $16\frac{5}{8}$ | (*a*) 7<br>(*b*) $5\frac{1}{4}$ | ... | $CO_2$ 14·6<br>$O_2$ 7·5<br>$N_2$ 77·9 |
| 9 | 1 | 30 | 222 | 346 | −1·3 | (*a*) $16\frac{3}{4}$<br>(*b*) 15 | (*a*) 5<br>(*b*) $3\frac{1}{2}$ | ... | $CO_2$ 16·9<br>$O_2$ 6·1<br>$N_2$ 77·0 |

TABLE II.—*Stove on Blast.*

| No. of Experiment. | Time. | | Average Hot Blast Temp. | Average Cold Blast Temp. | Average Blast Pressure in Lbs. per Sq In. | Hygrometer. | | Pitot Tube Head in Ins. w.g. | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Wet. | Dry. | Right-hand Main. | Left-hand Main. |
| | H. | M. | | | | | | | |
| 1 | 1 | 16 | 737 | 25 | 4·75 | 13·2 | 14·2 | 1·00 | 0·770 |
| 2 | 1 | 4 | 743 | 26 | 4·75 | 10·7 | 10·8 | 0·917 | 0·718 |
| 3 | 1 | 8 | 723 | 24 | 4·5 | 9·4 | 9·4 | 0·910 | 0·721 |
| 4 | 1 | 18 | 709 | 22 | 4·6 | 9·4 | 9·4 | 0·956 | 0·741 |
| 5 | 1 | 2 | 703 | 22 | 4·5 | 9·3 | 9·4 | 0·832 | 0·714 |
| 6 | 1 | 1 | 743 | 21 | 5·0 | 9·4 | 10·0 | 0·610 | 0·490 |
| 7 | 1 | 7 | 722 | 22 | 4·6 | 9·7 | 10·3 | 0·788 | 0·650 |
| 8 | 0 | 57 | 730 | 23 | 4·5 | 10·1 | 10·8 | 1·07 | 0·882 |
| 9 | 0 | 53 | 727 | 24 | 4·2 | 10·2 | 11·4 | 0·893 | 0·718 |

## CALCULATIONS.

### 1. *The Heat taken up by the Blast.*

It is first necessary to find the average velocity of the blast in each of the two mains during each experiment.

Considering the right-hand main in Experiment 1, we have—

Pressure of blast = 4·75 lbs. per square inch.
Temperature of blast = 25° C.

The weight of 1 cubic foot of air at this temperature and pressure = 0·09788 lbs.

In Griggs's formula—

$$V = 0{\cdot}997\sqrt{\frac{2ghw}{12d}}$$

$g = 32{\cdot}2$ ft./sec.
$h = 1{\cdot}00$ inches water gauge.
$w = 62{\cdot}4$ lbs.
$d = 0{\cdot}09788$ lbs.

$$\therefore\ V = 0{\cdot}997\sqrt{\frac{64{\cdot}4 \times 1{\cdot}00 \times 62{\cdot}4}{12 \times 0{\cdot}09788}}$$

$$= 58{\cdot}33 \text{ ft./sec.}$$

Since the area of each main = 2·281 square feet and the duration of Experiment 1 was 1 hour 16 minutes (= 4560 seconds), the amount of blast blown through the right-hand main

= 58·33 × 2·281 × 4560 = 606,800 cubic feet.

Similarly the blast blown through the left-hand main . . = 532,300 „ „

Total . . . = 1,139,100 cubic feet.

= 1,380,000 cubic feet at N.T.P.

The mean specific heat of air between 25° and 737° C. = 0·243.

1 cubic foot of air at N.T.P. requires 8·898 calories per ° C. rise in temperature.

∴ The heat required to raise 1 cubic foot of air from 25° C. to 737° C.

$$= \frac{712 \times 8{\cdot}898}{1000} = 6{\cdot}3354 \text{ K.C.U.'s.}$$

∴ The heat required to raise the temperature of the blast blown in Experiment 1

= 1,380,000 × 6·3354 = 8,744,000 K.C.U.'s.

The results for each experiment are given in the following table:—

TABLE III.

| No. of Experiment. | Velocity in ft./sec. | | Amount of Blast Blown. | | Total Cubic Feet. | Total at N.T.P. | No. of K.C.U.'s required to Raise the Temp. of Blast. |
|---|---|---|---|---|---|---|---|
| | Right-hand Main. | Left-hand Main. | Right-hand Main. | Left-hand Main. | | | |
| 1 | 58·33 | 51·17 | 606,800 | 532,300 | 1,139,100 | 1,380,000 | 8,744,000 |
| 2 | 55·94 | 49·49 | 490,100 | 433,600 | 923,700 | 1,116,000 | 7,119,000 |
| 3 | 55·90 | 49·76 | 520,400 | 463,300 | 983,700 | 1,181,000 | 7,347,000 |
| 4 | 56·96 | 50·13 | 608,200 | 535,300 | 1,143,500 | 1,390,000 | 8,498,000 |
| 5 | 53·27 | 49·35 | 452,200 | 418,800 | 871,000 | 1,053,000 | 6,380,000 |
| 6 | 44·94 | 40·29 | 375,300 | 336,400 | 711,700 | 885,000 | 5,690,000 |
| 7 | 51·70 | 46·96 | 474,200 | 430,800 | 905,000 | 1,100,000 | 6,852,000 |
| 8 | 61·93 | 54·94 | 483,300 | 428,700 | 912,000 | 1,098,000 | 6,908,000 |
| 9 | 55·84 | 50·05 | 405,200 | 363,200 | 768,400 | 908,000 | 5,682,000 |
| | | | | | Total . | 10,111,000 | 63,220,000 |

## 2. *The Heat taken up by the Moisture in the Blast.*

The average humidity of the air, deduced from the wet and dry bulb hygrometer readings taken during the test = 0·95,

whence—

The amount of water vapour per cubic metre of air = 9·0 grammes.

The amount of water vapour per cubic foot of air = 0·255 grammes.

The amount of water vapour per cubic foot of air at N.T.P. = 0·265 grammes.

The total volume of air used = 10,111,000 cubic feet.

∴ The amount of water entering the stove with the blast = 2679 kilogrammes.

The heat required to raise 2679 kilogrammes of water from 25° C. to 100° C. = 75 × 2679 = 200,900 K.C.U.'s.

The heat required to evaporate 2679 kilogrammes of water from and at 100° C. = 536 × 2679 = 1,436,000 „

The heat required to raise 2679 kilogrammes of steam from 100° C. to 727° C. = 627 × 2679 × 0·505 = 816,000 „

Total = 2,452,900 K.C.U.'s.

### 3. *The Sensible Heat of the Gas per Cubic Foot at N.T.P.*

The average composition of the gas is

| | Per Cent. |
|---|---|
| $CO_2$ | 9·5 |
| CO | 30·0 |
| $H_2$ | 1·0 |
| $N_2$ | 59·5 |

The mean specific heats of these gases between 0° C. and 250° C. are

| | |
|---|---|
| $CO_2$ | 0·222 |
| CO | 0·243 |
| $H_2$ | 3·410 |
| $N_2$ | 0·241 |

whence the heat required to raise 1 cubic foot of this gas 1° C.

= 8·984 calories = 0·008984 K.C.U.'s.

The average temperature of the gas = 240°.

∴ The sensible heat of the gas per cubic foot at N.T.P.

= 240 × 0·008984 K.C.U.'s

= 2·156 K.C.U.'s.

### 4. *The Heat of Combustion of the Gas per Cubic Foot at N.T.P.*

The heat of combustion of hydrogen per gramme-molecule

= 68·36 K.C.U.'s.

The heat of combustion of carbon-monoxide per gramme-molecule

= 67·96 K.C.U.'s.

Whence the heat of combustion of blast-furnace gas of the composition given above = 27·54 K.C.U.'s per cubic foot at N.T.P.

### 5. *The Heat carried off by the Products per Cubic Foot (at N.T.P.) of Gas burnt.*

The average analysis of the products of combustion is

| | Per Cent. |
|---|---|
| $CO_2$ | 15·2 |
| $O_2$ | 7.4 |
| $N_2$ | 77·4 |

For perfect combustion we should have

| | *Gas.* | | *Products.* | |
|---|---|---|---|---|
| $CO_2$ . . | 9·5 | $CO_2$ . . | 9·5 | |
| $CO$ . . | 30·0 + [15$O_2$ + 60 $N_2$] | $CO_2$ . . | 30·0 + $N_2$ | 60·0 |
| $H_2$ . . | 1·0 + [ ½$O_2$ + 2 $N_2$] | | $N_2$ | 2·0 |
| $N_2$ . . | 59·5 | | $N_2$ | 59·5 |
| | 100·0 | $CO_2$ . . | 39·5 + $N_2$ | 121·5 |

15·2 cubic feet of $CO_2$ are contained in 100 cubic feet of products.
∴ 39·5 ,, ,, ,, ,, 260 ,, ,,
*i.e.* every 100 cubic feet of gas burnt yields 260 cubic feet (at N.T.P.) of products.

But for perfect combustion every 100 cubic feet of gas gives 161 cubic feet of products.

∴ Excess air per 100 cubic feet of gas = 99 cubic feet.

(A) *The Heat required to raise the Temperature of the Excess Air.*

Initial air temperature. . . . . . . = 15°
Average temperature of flue products . . = 366°

∴ The heat required to raise the temperature of the excess air

$$= 0{\cdot}99 \times 28{\cdot}32 \times 1{\cdot}2931 \times 0{\cdot}237 \times 0{\cdot}351$$

= 3·015 K.C.U.'s per cubic foot (at N.T.P.) of gas burnt.

(B) *The Heat contained in the Theoretical Products of Combustion.*

Every 100 cubic feet of gas burnt yields

$$\left.\begin{array}{l} 39{\cdot}5 \text{ cubic feet of } CO_2 \\ 121{\cdot}5 \quad ,, \qquad ,, \qquad N_2 \end{array}\right\} \text{at N.T.P.}$$

The sensible heat contained in these at 366° C. is

$$\begin{array}{ll} CO_2 & 39{\cdot}5 \times 28{\cdot}32 \times 1{\cdot}9651 \times 0{\cdot}227 \times 0{\cdot}366 \text{ K.C.U.'s.} \\ N_2 & 121{\cdot}5 \times 28{\cdot}32 \times 1{\cdot}2514 \times 0{\cdot}242 \times 0{\cdot}366 \quad ,, \end{array}$$

Total = 5·641 K.C.U.'s.

∴ The total heat carried off by the products of combustion = 8·656 K.C.U.'s per cubic foot (at N.T.P.) of gas burnt.

Now if $x$ = the number of millions of cubic feet (at N.T.P.) of gas burnt during the whole trial

Then the total heat put into the stove is made up of

| | |
|---|---|
| The sensible heat in the gas . | 2·156$x$ million K.C.U.'s |
| The heat of combustion of the gas . . . . . | 27·54$x$ ,, ,, |
| Total . . | 29·696$x$ million K.C.U.'s |

The total heat obtained from the stove is made up of

| | | | |
|---|---|---|---|
| The sensible heat in the products . . . . | 8·656$x$ million | K.C.U.'s | |
| The heat taken up by the blast . . . . | 63·220 | ,, | ,, |
| The heat taken up by the moisture in the blast . | 2·453 | ,, | ,, |
| The heat lost by radiation (say 5 per cent.) . . | $\frac{1}{20}\times 29{\cdot}696x$ | ,, | ,, |
| Total . . | 10·141$x$ + 65·673 million | K.C.U.'s | |

$$\therefore\ 29{\cdot}696x = 10{\cdot}141x + 65{\cdot}673,$$

$$x = 3{\cdot}359.$$

This gives for the heat balance of the stove—

*Credit Side.*

| | Per Cent. |
|---|---|
| Sensible heat in the gas . | 7·3 |
| Heat of combustion of the gas . . . . . | 92·7 |
| | 100·0 |

*Debit Side.*

| | Per Cent. |
|---|---|
| Heat taken by blast . | 63·3 |
| Heat taken by moisture in blast . . . | 2·6 |
| Heat taken off by products | 29·1 |
| Heat lost by radiation . | 5·0 |
| | 100·0 |

My thanks are due to the Skinningrove Iron Co. Ltd., for the facilities given me in carrying out this investigation, and to Prof. W. A. Bone, F.R.S., for his valuable advice and criticism.

# PRELIMINARY REPORT ON THE HEAT BALANCE OF STEEL FURNACES.

By R. S. G. KNIGHT, B.Sc. (London).

## The Design of an Experimental Furnace.

This furnace is designed for testing the efficiency of regeneration of the air and gas, either singly or combined, used for firing. The arrangement permits of its use either (*a*) as an open-hearth furnace fired on the Bonecourt surface combustion principle, or (*b*) as a muffle furnace fired either on the Bonecourt system or by a series of J. Wright flame burners. The alterations necessary for changing from one type of furnace to another or from one method of firing to another are quite simply effected, as will be afterwards described in dealing with the detailed experiments.

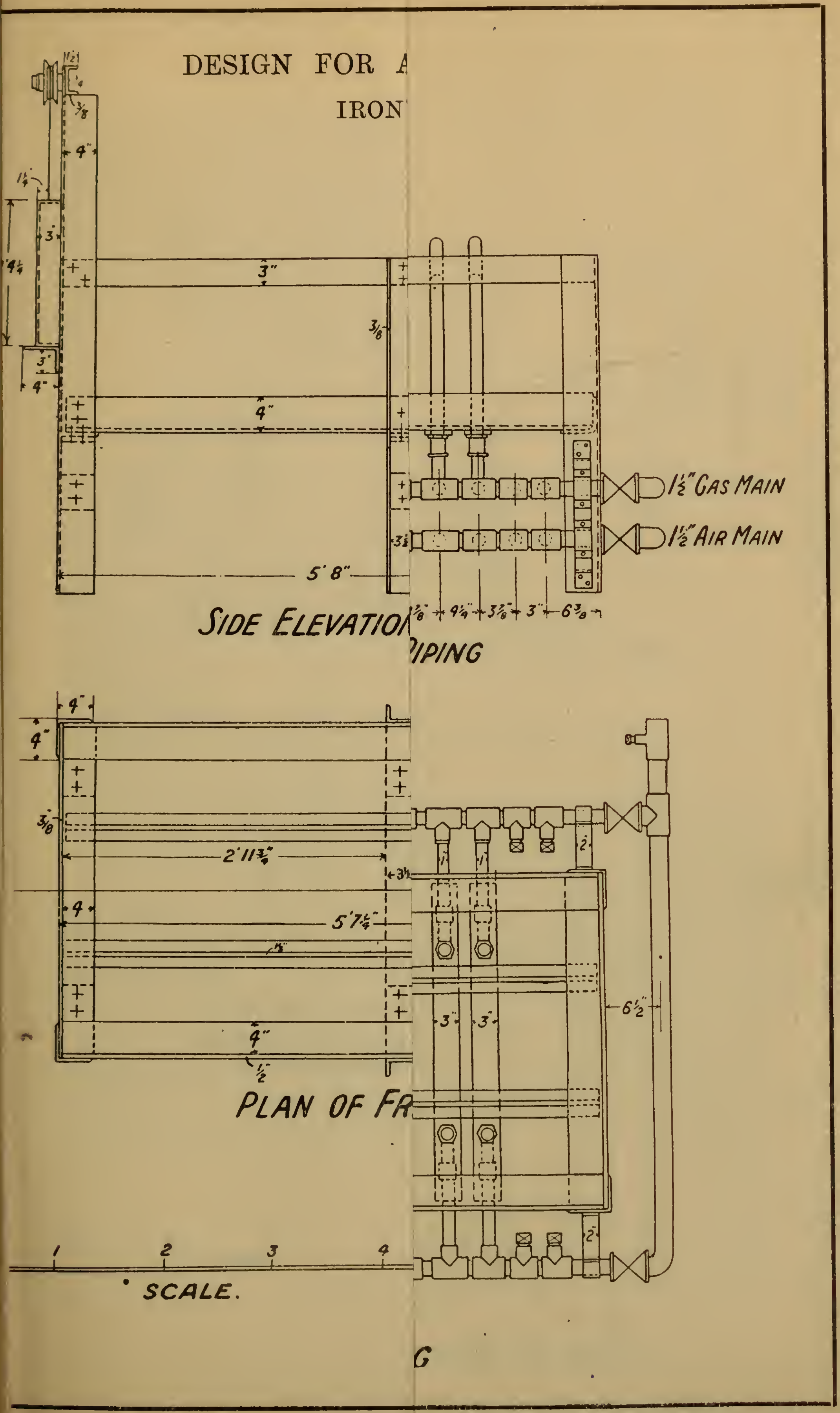
The gas used can either be the gas supplied by the Gas Light and Coke Company or washed Mond producer-gas from the plant erected at the Imperial College, or a mixture of the two in any proportions.

The arrangement of the framework of the furnace is shown in Plate X. It consists essentially of two parts, the furnace proper and the regenerator. The latter contains the solid-drawn steel regenerator tubes, provision being made for any number up to six, arranged in parallel in order to provide for different degrees of regeneration. The regenerators can be connected up with either the gas or air mains or with both at once, according as it is desired to regenerate the air or the gas or a mixture of both. Since the air and gas mains are taken along the back and both sides of the furnace, it is possible to fire from either side as required.

The furnace portion of the framework contains the burners. The air and gas are led into three mixing tubes running across the furnace, from each of which four burners are taken. When the furnace is used as an open-hearth furnace the outer rows only are required, the inner rows being called into

DESIGN FOR A

IRON


1½"
¼
⅜
4"
1¼"
3
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3"
4"
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4"
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5' 8"
1½" Gas Main
1½" Air Main
⅞ 9¼ 3⅞ 3" 6⅜
SIDE ELEVATIO
IPING
4"
4"
⅜
2' 11¾"
3½
4
5' 7¼"
5"
4"
½
1"
1"
2
3"
3"
6½"
2"
PLAN OF FR
1
2
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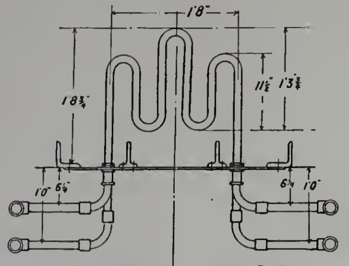
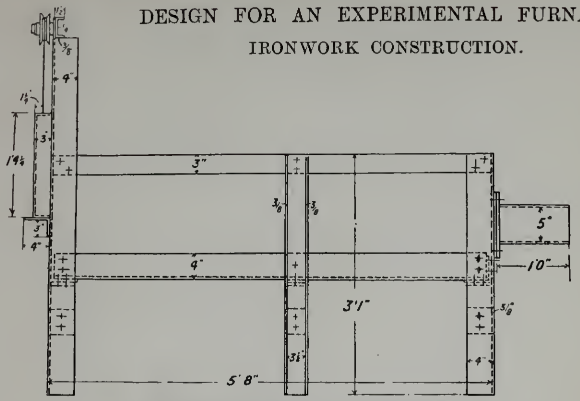
SCALE.
G

# DESIGN FOR AN EXPERIMENTAL FURNACE.

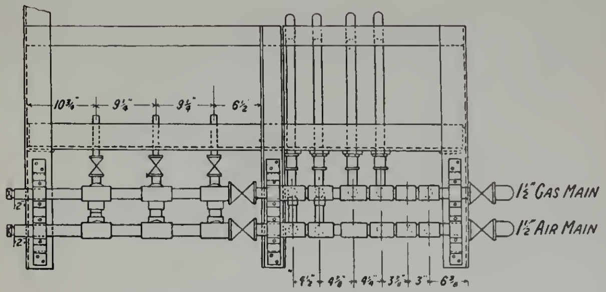
## IRONWORK CONSTRUCTION.


1'8"
1'8¾
11½"
1'3¾
1'0"
6¼
6¼
1'0"

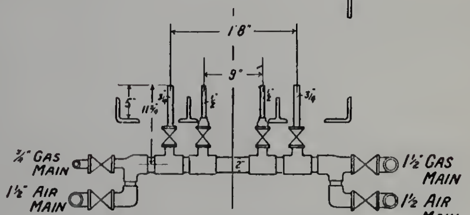
SECTION ON LINE C-D
SHOWING ONE AIR REGENERATING PIPE-AND ONE GAS REGENERATING PIPE.


1½
⅜
9"
1¼
3"
1'9¼
3"
4"
3"
4"
⅜
⅜
5"
1'0"
3'1"
⅜
3½
4"
5' 8"

SIDE ELEVATION OF FRAMEWORK.


10¾"
9¼"
9¼"
6½"
2"
2"
1½" GAS MAIN
1½" AIR MAIN
9½
9½
9¼
3½
3"
6⅜

SIDE ELEVATION OF PIPING


1'8"
9"
5"
11¾
¾
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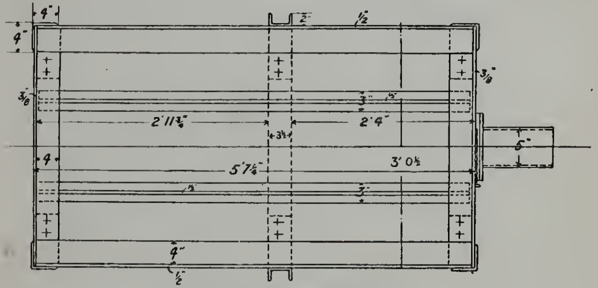
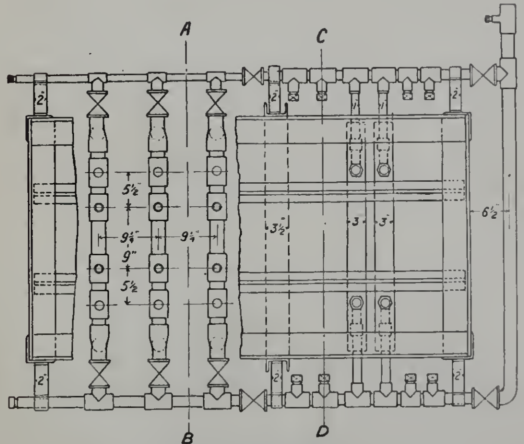
½
¾
2"
¾" GAS MAIN
1½" AIR MAIN
1½" GAS MAIN
1½" AIR MAIN

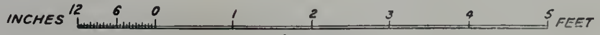
SECTION ON LINE A-B.
SHOWING ONE SET OF BURNERS AND ONE MIXING TUBE.


4"
4"
2"
½
⅜
⅜
2'11¾"
3½
2'4"
6"
4
5'7¼"
3'0½
3"
3"
4"
½

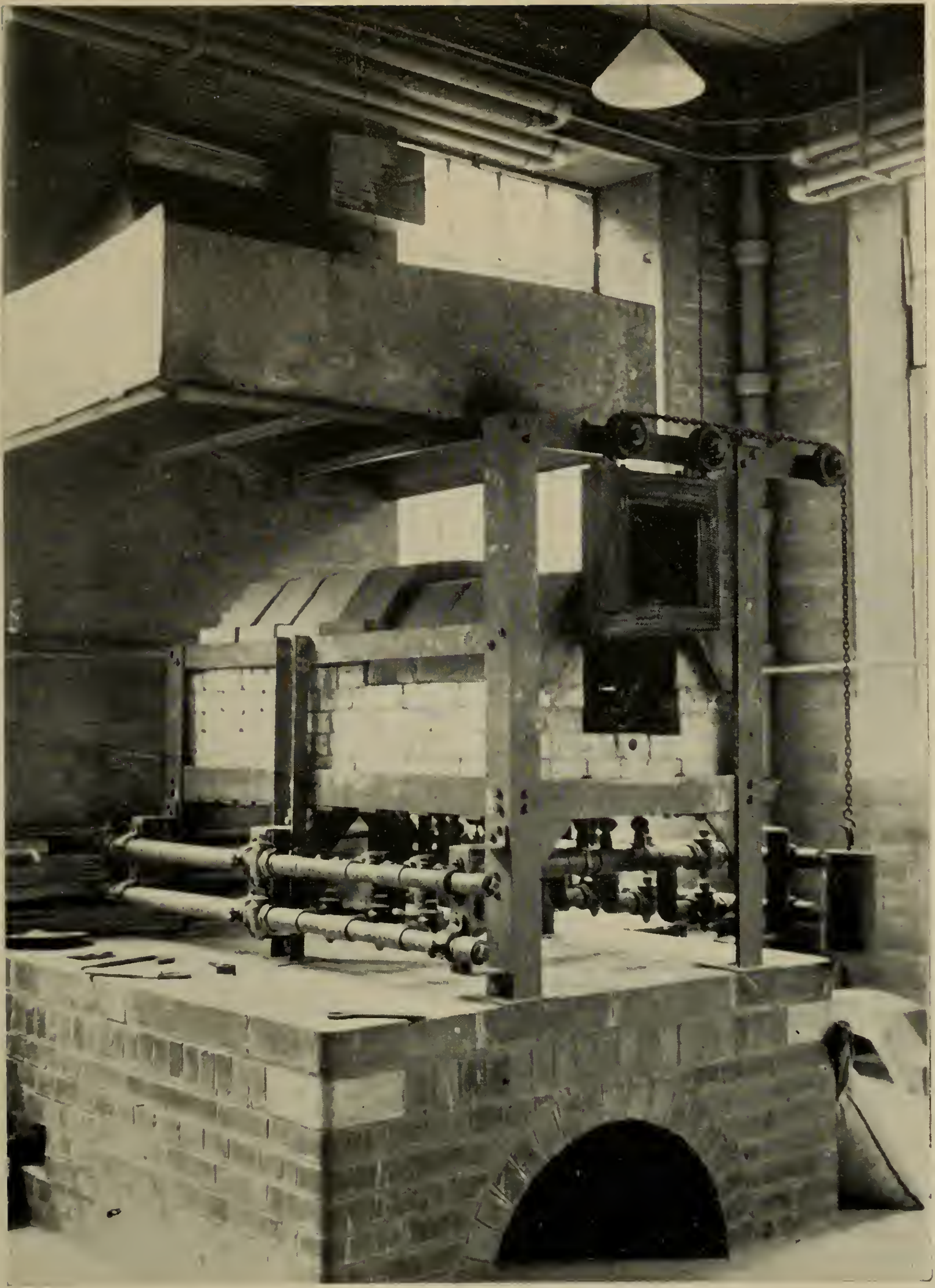
PLAN OF FRAMEWORK


A
C
2"
2"
2"
5½
9¼
9"
9¼
5½
3½
3
3
6½
2"
2"
2"
B
D

PLAN OF PIPING


INCHES
12
6
0
1
2
3
4
5
FEET

SCALE.



EXPERIMENTAL FURNACE.

play when the furnace is used as a muffle furnace. The amount of air and gas used, together with the mixing and the amount of mixture supplied to each burner, are all carefully controlled by cocks.

The sizes of the mains, mixture jets, and regenerator tubes are all obtained by calculations based on reasonable assumptions.

The sides, front, and back of the furnace are built of best Battersea Triangle brand firebricks supplied by the Morgan Crucible Company, whilst the roof is made of seven large firebrick arches fitting closely together and set with fireclay cement. Between the furnace proper and the regenerator a wall is built with openings at the top through which the hot products pass from the furnace, thus heating up the regenerator tubes to a high temperature. The exit gases are pulled through the flue pipe into the ventilating shaft by a fan situated on the roof at the top of the shaft.

The front of the furnace is closed by a door suspended by chains running over pulleys, a counterweight being attached to the free end of the chain to enable the door to be kept in any position desired.

The temperature of the inlet air and gas is taken by thermometers fixed in the mains near the furnace, whilst the temperature of the regenerated air or gas and also that of the flue products is taken by thermo-couples wired up to a Thread Recorder supplied by the Cambridge Scientific Instrument Company. From the flue a connection is run to a Bi-meter $CO_2$ recorder, so that the condition of combustion can be seen at any moment. A separate connection is, however, provided for the collection of an average sample of the products for accurate analysis.

The amount of gas used is measured by a special Parkinson and Cowan high-pressure meter, the indicated readings of which are compensated for any pressure up to 7 lbs.

The fitting of the furnace thus enables all the experimental data required in the calculation of the heat balance under any of the conditions of use, and with any of the methods of firing suggested, readily to be obtained.

The general appearance of the furnace erected ready for use is shown by the photograph reproduced as Plate XI.

# INVESTIGATION OF THE RELATIVE MERITS OF VARIOUS AGENTS FOR THE DEOXIDATION OF STEEL.[1]

By H. M. BOYLSTON (Cambridge, U.S.A.).

Few problems in the steel industry have been the subject of more investigation than that of making sound ingots or castings, and the means of preventing blowholes have been widely studied in this connection. Whether made by the crucible, the Bessemer, or the open-hearth processes, steel when cast is subject to blowholes, and various devices have been employed, and all kinds of "physic" added, to prevent the occurrence of these cavities, which exist sometimes near the surface and sometimes near the centre of the cast metal, rendering it in most cases of little value for castings and for large ingots except where the carbon content is low. The cause of these cavities has generally been associated in most minds with the presence of oxides of iron, and the materials used for their prevention have therefore come to be known as deoxidisers.

In a later report the author hopes to include a digest of previous work done along this line, the results of which have been published. Most of it has been carried out in a haphazard fashion, although several valuable papers have been based on scientific research. These are, however, comparatively recent, and refer rather to the chemical analysis of the gases existing in molten steel than to any attempt to find a remedy for preventing the formation of blowholes.

Most researches also have compared steel made with manganese additions, either with or without silicon, with similar steel to which aluminum has been added. Other researches have compared similar steel with steel to which titanium has been added, &c.

It seemed desirable, therefore, to compare directly the effect of the more ordinary so-called deoxidisers in order to furnish

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[1] Report received March 27, 1915.

a scientific basis, first, for detailed experiment in any particular case, and secondly to obtain a rough approximation of the relative merits of different agents. The fact that all the substances used for this purpose have a great affinity for oxygen is further evidence that most metallurgists have recognised the influence of oxygen on blowhole formation.

The author realises that the terms deoxidiser and deoxidation may be open to criticism. The terms solidifier and degasifier have suggested themselves, but although gases other than oxygen probably play considerable part in the formation of blowholes, he believes that the term deoxidiser is so well established in its special meaning that it is the best word to use in connection with this research.

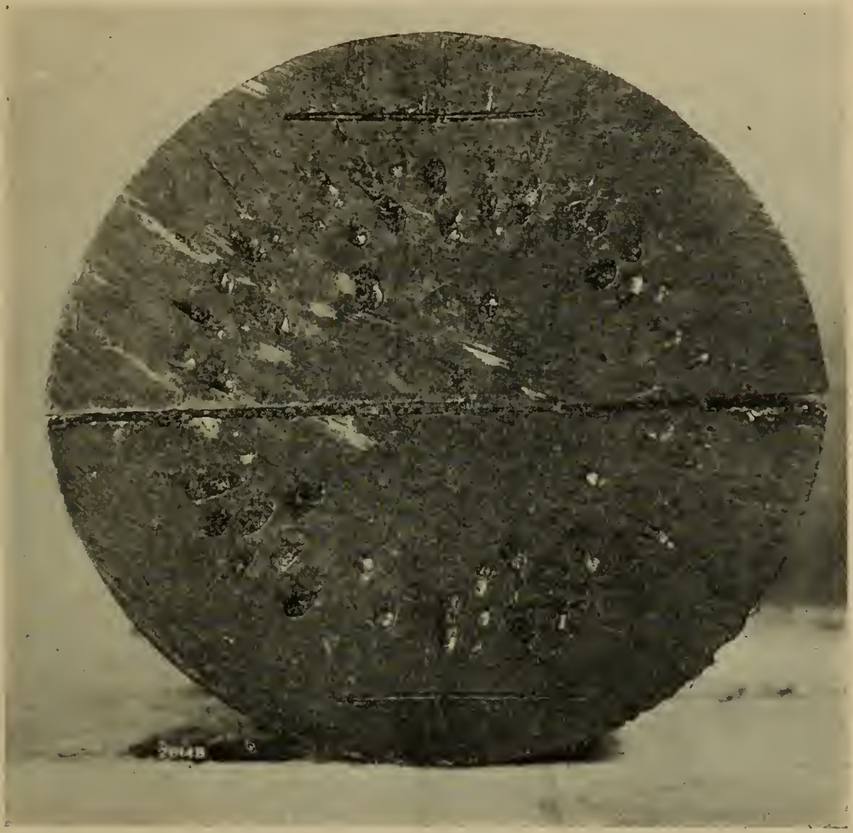

FIG. 1.

Raw Converter Metal. Transverse section at cropping point. Half size.

*Object of the Research.*—The chief object of this research is to ascertain the effect of the various commercial deoxidisers in rendering steel sound, especially as regards blowholes, and in removing oxides of iron which render steel red-short and unforgeable, as Bessemer found in his early experiments. The prevention of piping is not considered here except incidentally, since this defect can generally be prevented by physical means—such, for instance, as keeping the top of the ingot hot, and fluid compression. It should of course be borne in mind that a reagent may render an ingot or casting perfectly sound as regards blowholes while adding material in the way of by-products of deoxidation which would affect the physical properties of the metal. Hence the physical properties will be taken into account in this research.

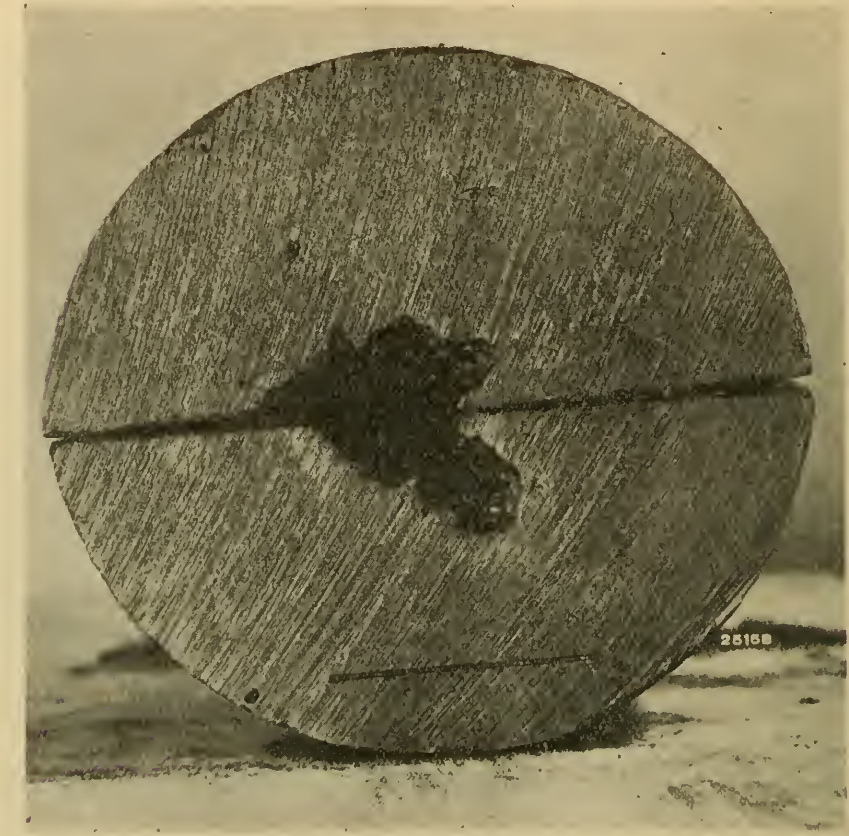

Fig. 2.

Raw Converter Metal with 0·05 per cent. Aluminium.

Transverse section at cropping point. Half size.

*Choice of Steel-making Process.*—A Tropenas 2-ton converter was available for this work, and it was not easy to make arrangements for the use of any other type of furnace. The choice was therefore controlled by practical considerations, yet as the Bessemer process is the one which gives the most highly oxidised product, perhaps, of any of the ordinary processes, it is possible, by exaggerating the oxidising conditions by the use of this method, as well as by overblowing the metal, to create conditions in which deoxidising conditions can be studied more effectively. It should not, therefore, be inferred that the results obtained in these experiments are directly applicable in detail to all methods of steel-making, especially in regard to the proportion of deoxidiser added, but the author hopes that the results will point the way to

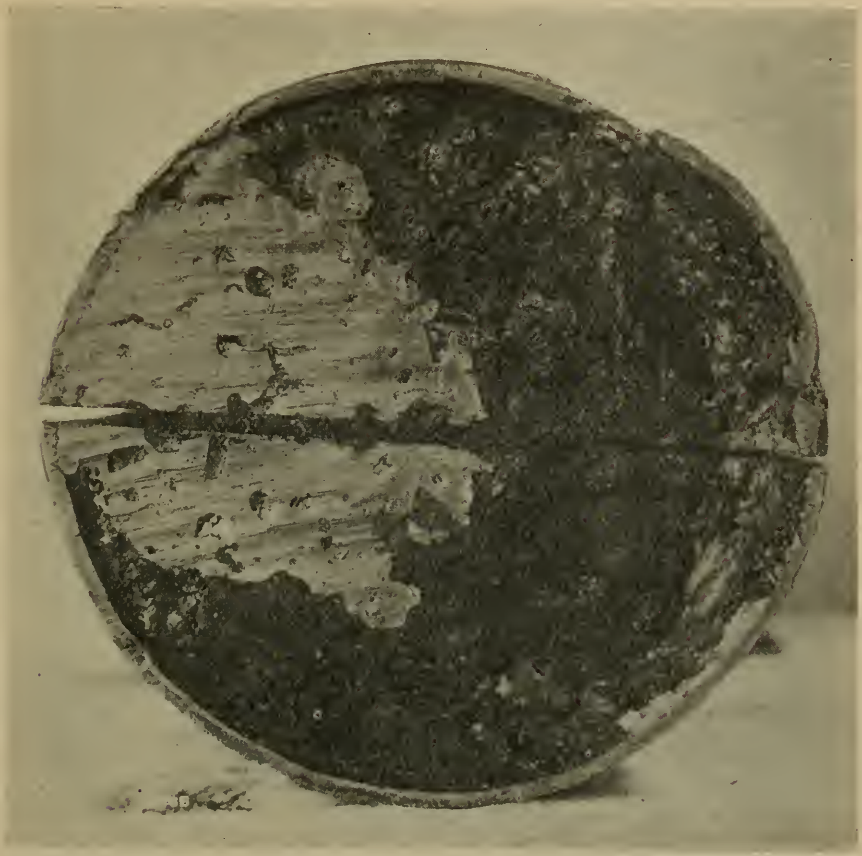

FIG. 3.

Raw Converter Metal with about 18 lbs. Washed Metal containing 3·46 per cent. Carbon. Transverse section at cropping point. Half size.

similar work with other steel processes, notably the basic open-hearth, which produces the largest tonnage of any, at least in the United States.

*General Plan.*—It was decided that the effect of the various deoxidisers on raw converter metal should first be determined, in order to select the proportion of each to be used for comparison with each other in the making of actual steel. Much thought was given to the selection of the proportions to be added. Where obtainable the advice of the manufacturer of the deoxidiser was followed fairly closely, and in all cases the advice of numerous well-known metallurgists and steel men was taken. It was finally decided to cast seventy-two ingots

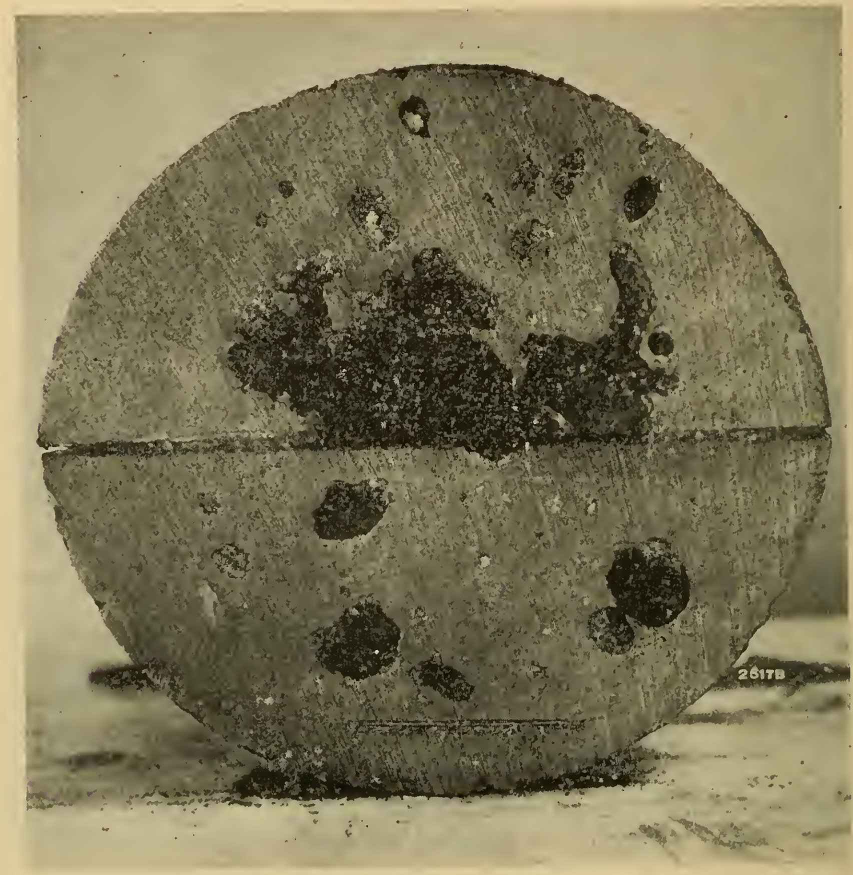

FIG. 4.

Raw Converter Metal with 0·05 per cent. Aluminium and about 18 lbs. Washed Metal containing 3·46 per cent. Carbon. Transverse section at cropping point. Half size.

of raw metal (from the Tropenas converter), to which the various proportions of the different deoxidisers were to be added. Four proportions of each were used, and the ingots were made in triplicate, the object being merely to determine which of the four gave the soundest ingot as measured by density and the appearance of a section. Vertical sections would have been more valuable than transverse, but their cost made them impracticable. The second experiment included fifteen ingots of commercial steel from one heat, to which were added the proportions of each deoxidiser which were found to give the best results in Experiment 1. The ingots in Experiment 2 were subjected to a more complete examination, tests being made for density, porosity, tenacity, and ductility, in both cast and forged metal after annealing.

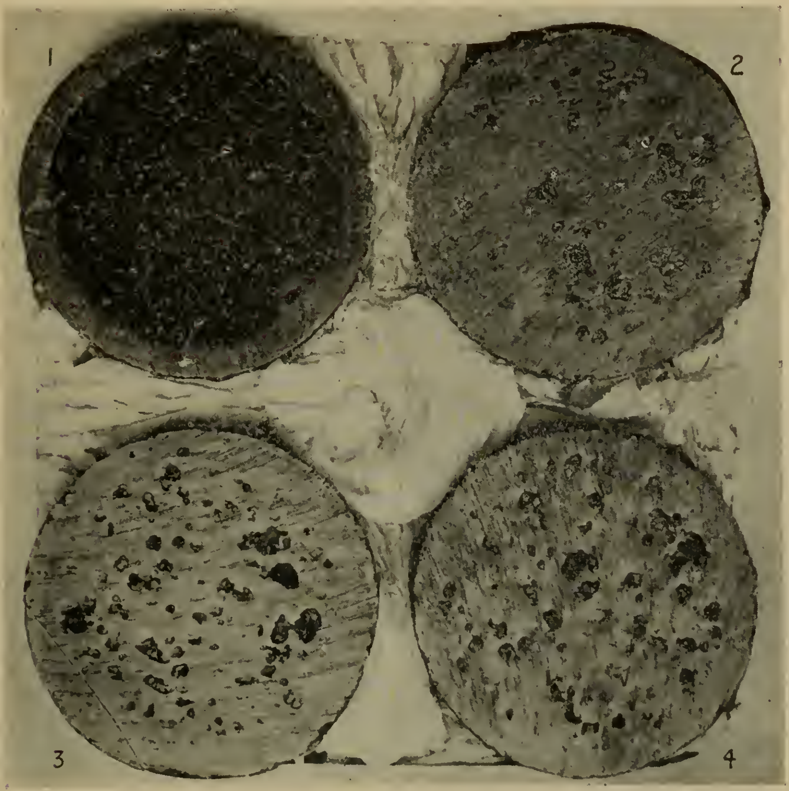

FIG. 5.

Ingots 1 and 2 with 0·03 per cent. Titanium. Ingots 3 and 4 with 0·045 per cent. Titanium. Transverse section at cropping point one-fourth actual size. Addition used—15 per cent. ferro-carbon titanium.

All ingots were cast in a steel foundry under works conditions.

*Details of Procedure.*—The first plans called for the use of steel (as opposed to raw converter metal) for Experiment 1, and the method was to add washed metal to bring up the carbon content.

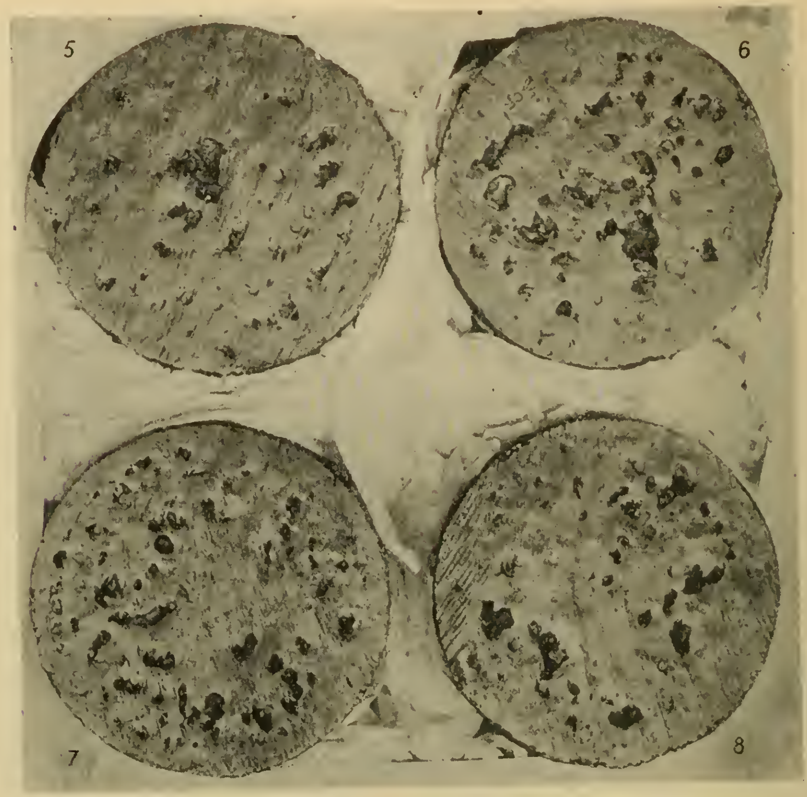

FIG. 6.

Ingots 5 and 6 with 0·06 per cent. Titanium. Ingots 7 and 8 with 0·10 per cent. Titanium. Transverse section at cropping point one-fourth actual size. Addition used—15 per cent. ferro-carbon titanium.

Several preliminary experiments were therefore made to find out what deoxidising or solidifying effect the washed metal itself might have, in order to decide the order in which the deoxidiser and the recarburiser should be added. Twelve ingots, weighing about 150 lbs. each, were poured, two of these being (1) raw converter metal, and the other ten having added to them (2) aluminium only, (3) washed metal only, (4) aluminium and washed metal, (5) washed metal and then aluminium. In most cases more than one ingot was made with a given addition.

In Figs. 1 to 4 inclusive are shown photographs, about one-half natural size, of ingots representing the first four of these classes in transverse section at the point of cropping.

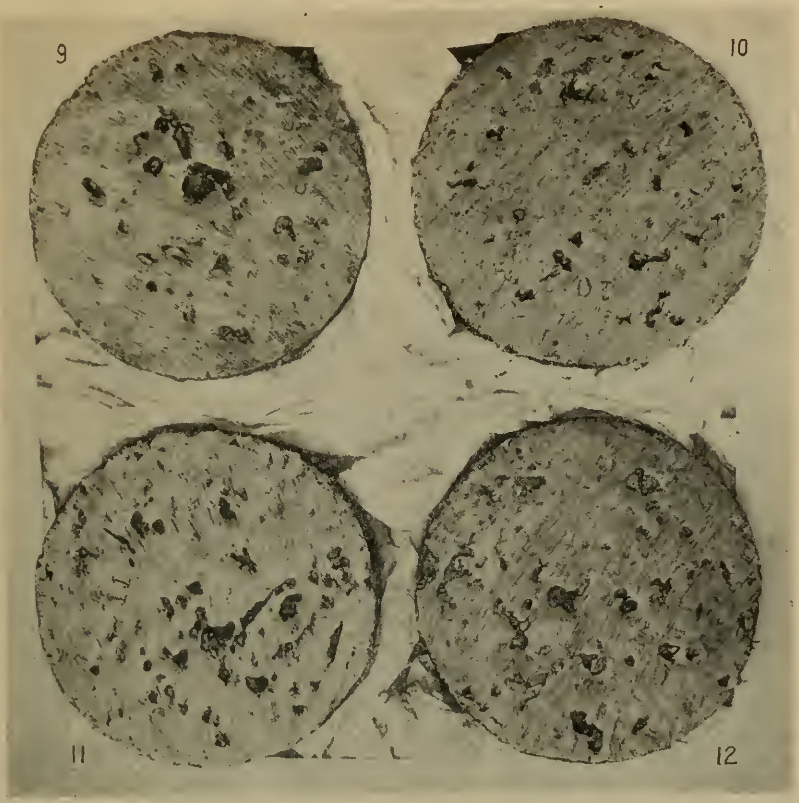

FIG. 7.

Ingots 9 and 10 with 0·01 per cent. Titanium. Ingots 11 and 12 with 0·02 per cent. Titanium. Transverse section at cropping point one-fourth actual size; 25 per cent. carbon-free ferro-titanium.

The amount of carbon in these ingots is shown below.

*Carbon Content of Preliminary Ingots.*

| Ingot No. | Illustration. | Per Cent. of Carbon. |
|---|---|---|
| 1 | Figs. 1 and 5 | 0·184 |
| 2 | ,, 2 and 6 | 0·170 |
| 3 | ,, 3 and 7 | 0·33 |
| 4 | ,, 4 and 8 | 0·314 |

It is interesting to note the comparative solidity of the raw converter metal cast without additions, but it must be remembered that this metal contained about 0·184 per cent. carbon, and could therefore hardly have been as much overblown as was intended. This is verified by the casting notes, which state that the metal was very slightly overblown. The additions of aluminium, either alone or with washed metal added later (Figs. 2 and 4), produced a deep pipe but no blowholes, whereas when washed metal alone was added an extremely spongy ingot was produced.

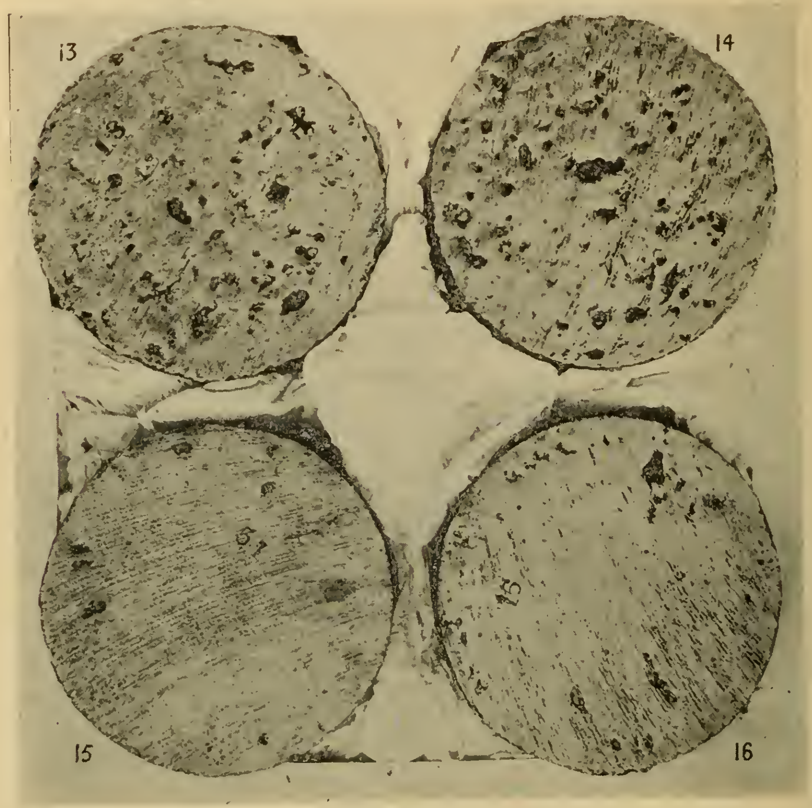

FIG. 8.

Ingots 13 and 14 with 0·03 per cent. Titanium. Ingots 15 and 16 with 0·10 per cent. Titanium. Transverse section at cropping point one-fourth actual size; 25 per cent. carbon-free ferro-titanium.

These preliminary ingots suggested that it might be well to make an experiment with commercial steel, adding the deoxidisers before making the usual additions of carbon, manganese, and silicon.

It was finally decided to perform Experiment 1 with raw metal instead of recarburised metal, so that a direct measure might be obtained of the deoxidising and solidifying effect of the additions under test.

*Proportion of Ferro-Carbon Titanium.*—In order to determine what should be the largest proportion of ferro-carbon titanium to be added, and whether the additions should be preheated, three preliminary ingots were poured, the first being plain converter metal to check the previous results, the second containing about 4 lbs. of 15 per cent. ferro-carbon titanium in very small pieces but not preheated, while to the third was added the same amount of 15 per cent. ferro-carbon titanium which had been pre-heated to redness, using a smoky oil flame. The inten-

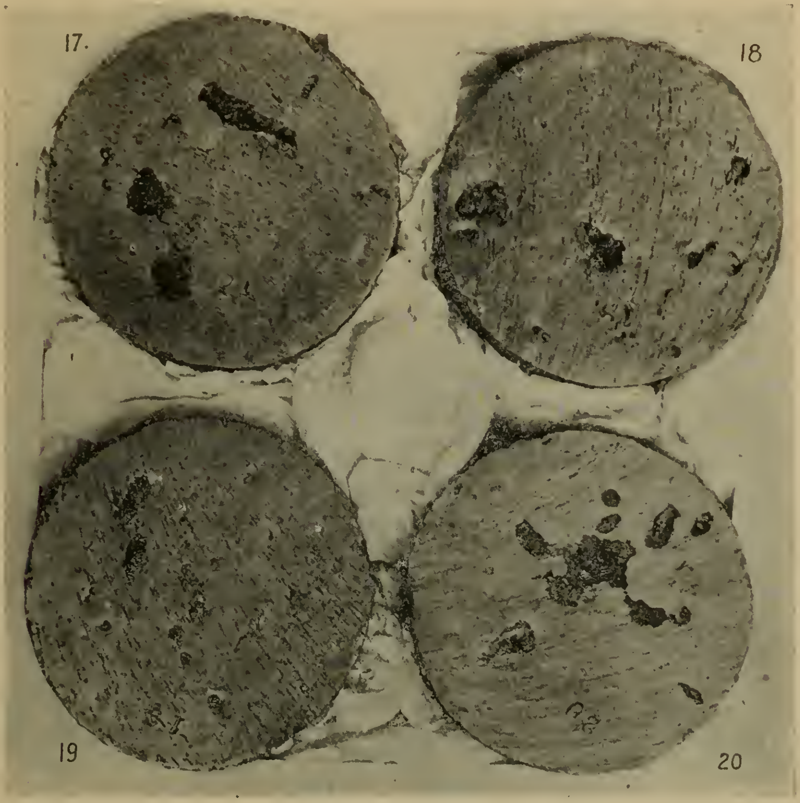

FIG. 9.

Ingots 17 and 18 with 0·20 per cent. Silicon. Ingots 19 and 20 with 0·30 per cent. Silicon. Transverse section at cropping point one-fourth actual size.

tion was to add 0·3 per cent. metallic titanium. Ingot No. 1 checked the previous results with plain converter metal very closely. In Ingot No. 2 there was a considerable quantity of frozen material left in the hand ladle, and in both Ingots 2 and 3 most of the ferro-carbon titanium floated to the top and apparently was not absorbed. It was decided to use

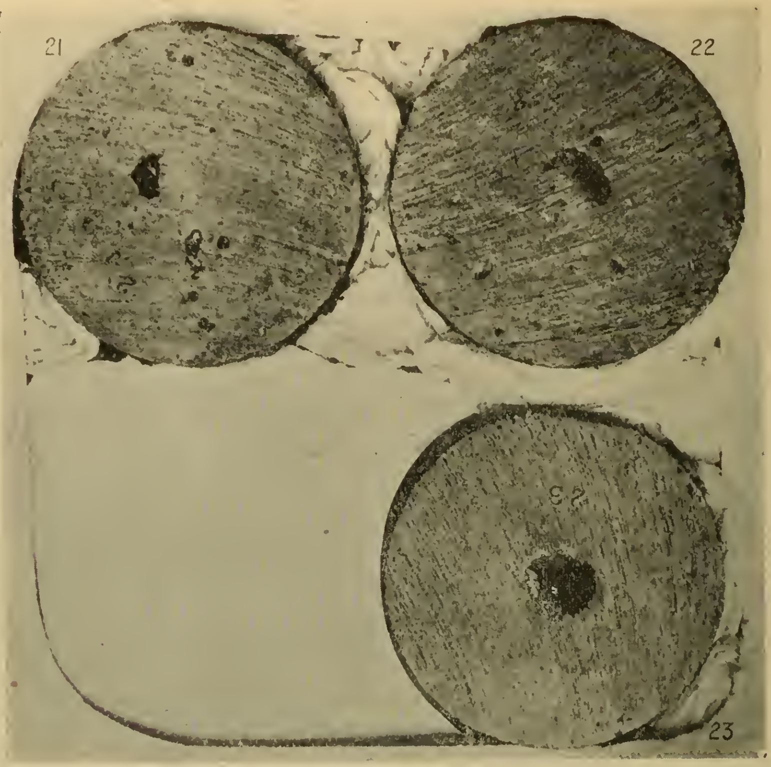

FIG. 10.

Ingots 21 and 22 with 0·40 per cent. Silicon. Ingots 23 and 24 with 0·50 per cent. Silicon. Transverse section at cropping point one-fourth actual size.

0·1 per cent. titanium in the form of the 15 per cent. alloy as the maximum, and that with this smaller amount it need not be preheated. It should here be added that most of the published results where titanium has been used in steel mention 0·1 per cent. titanium or less as the addition. The amount recommended by the manufacturers for commercial use is 0·1 per cent.

## PROCEDURE IN EXPERIMENT 1.

The steel was cast in three heats, twenty-four ingots to a heat.

The converter metal, after being somewhat overblown, was slagged off and poured into preheated clay-lined crucibles which served as hand ladles. The additions had been previously carefully weighed out to the nearest half ounce in paper bags.

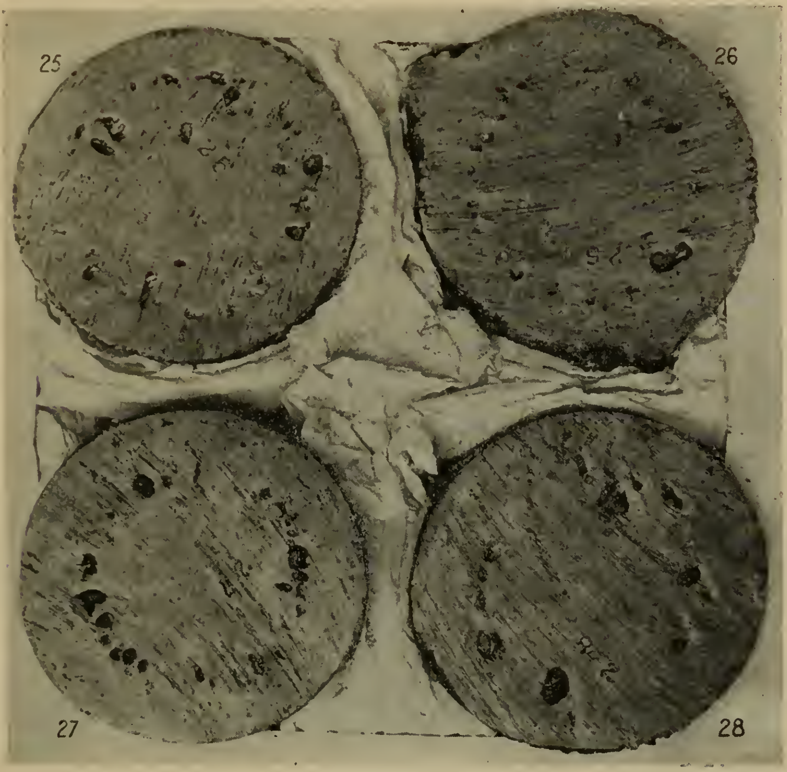

FIG. 11.

Ingots 25 and 26 with 0·50 per cent. Manganese. Ingots 27 and 28 with 0·75 per cent. Manganese. Transverse section at cropping point one-fourth actual size.

*Moulds.*—These were of sand carefully baked, and arranged as far as possible in one large flask for convenience. The dimensions of the moulds were such as to accommodate an ingot 20 inches high by 6 inches in diameter. The moulds were made by skilled moulders according to the usual works practice at Watertown Arsenal, Watertown, Mass.

*Casting.*—Steel was blown, slagged off, and poured by the men employed for this purpose at the Arsenal, and a large force was used in order to handle the ladles rapidly. The steel was poured from the large ladle into the hand ladles by tilting, and the proper amount of metal was ascertained by filling the ladle to a certain mark made previously. The endeavour was to have the ingots all, as near as possible, of the same size. On account of the small size of ingot, it was found impracticable to weigh the metal each time for fear of sculling. The deoxidisers were all weighed and added to the metal by the author.

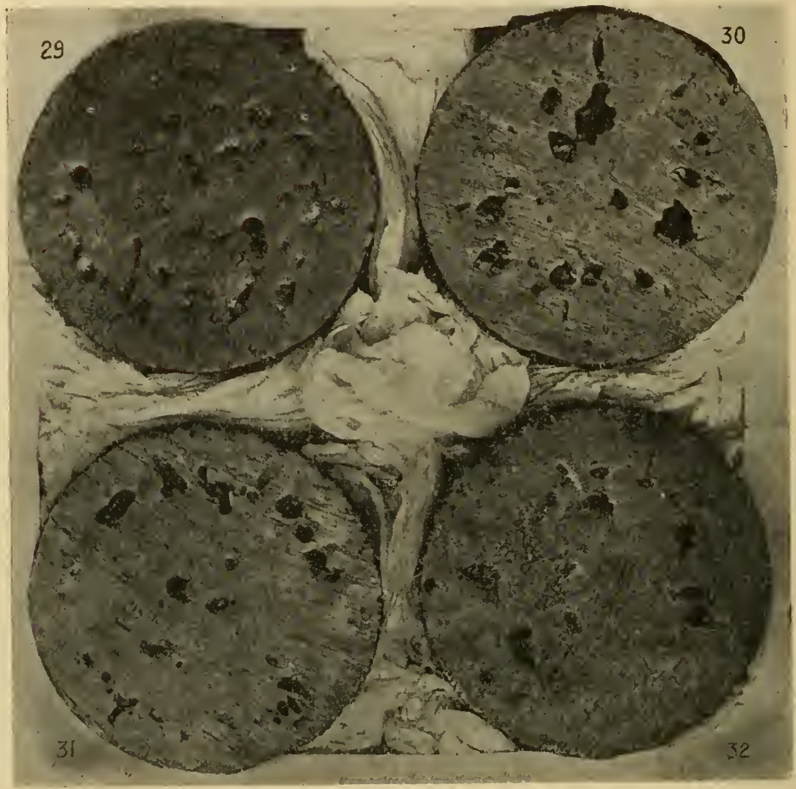

FIG. 12.

Ingots 29 and 30 with 1·00 per cent. Manganese. Ingots 31 and 32 with 1·25 per cent. Manganese. Transverse section at cropping point one-fourth actual size.

Table I. gives the records of the heats. It was attempted to hold the metal in the crucible for two minutes after making the addition, but it was soon found that this was impracticable, and it will be seen from the table that most of the castings were held from one-half to one minute after the additions were made.

TABLE I.—*Heat Records in Experiment* 1.

| Ingot No. | Time into Hand-ladle. | Time of Holding in Hand-ladle. | | Temperature of Pouring, Degrees C. | Condition of Metal. | Remarks. |
|---|---|---|---|---|---|---|
| | A.M. | Min. | Sec. | | | *First Blow.* |
| 1 | 11.28 | 1 | 23 | 1560 | Hot | Blown at 11-20-05. |
| 2 | 11.29 | 1 | 30 | 1375 | ,, | Overblown at 11-20-18. |
| 3 | 11.33 | 1 | 27 | 1388 | ,, | Down at 11-20-30. |
| 4 | 11.34 | 2 | 03 | 1375 | ,, | Into ladle 11-23-20. |
| 5 | 11.37 | 1 | 08 | 1375 | Freezing | Scull removed 11-36-10. |
| 6 | 11.39 | 1 | 02 | 1382 | ,, | Began pouring 11-37-30. |
| 7 | 11.42 | 1 | 03 | 1365 | Hot | Chem. cup sample taken 11-39-40. |
| 8 | ... | 0 | 59 | 1365 | ,, | |
| 9 | ... | 0 | 48 | 1355 | Cold | The discrepancies in time are accounted for by the fact that several observers were working and their watches did not agree exactly. |
| 10 | 11.44 | 0 | 48 | 1365 | Hot | |
| 11 | 11.47 | 0 | 45 | 1365 | ,, | |
| 12 | ... | 0 | 46 | 1355 | ,, | |
| 13 | 11.50 | 0 | 51 | 1340 | ,, | |
| 14 | ... | 0 | 45 | 1340 | ,, | |
| 15 | 11.52 | 0 | 47 | 1340 | Froze | |
| 16 | ... | 0 | 49 | 1330 | ,, | |
| 17 | 11.54 | 0 | 55 | 1340 | Good | |
| 18 | 11.54 | 0 | 50 | 1330 | Cold | |
| 19 | 11.57 | 0 | 37 | 1340 | Hot | |
| 20 | 11.57 | 0 | 30 | 1330 | ,, | |
| 21 | 11.59 | 0 | 29 | 1330 | ,, | |
| 22 | 12.00 | 0 | 33 | 1330 | ,, | |
| 23 | 12.02 | 0 | 25 | 1330 | Cold | 34 minutes to cast 23 ingots. |
| 24 | | Lost—Too Cold. | | | | |
| | P.M. | Min. | Sec. | | | *Second Blow.* |
| 25 | 1.30 | 0 | 46 | 1355 | Hot | Blown at 1-20-0. |
| 26 | 1.31 | 0 | 47 | 1355 | ,, | Into ladle 1-23-30. |
| 27 | 1.31 | 0 | 58 | 1355 | ,, | Sculled 1-26-20. |
| 28 | 1.31 | 0 | 45 | 1355 | ,, | Began pouring 1-28-0. |
| 29 | 1.33 | 1 | 8 | 1355 | ,, | |
| 30 | ... | 0 | 48 | 1355 | ,, | |
| 31 | ... | 0 | 45 | 1355 | ,, | |
| 32 | 1.35 | 0 | 46 | 1355 | ,, | Spilled. |
| 33 | ... | 0 | 55 | 1355 | Hot | |
| 34 | ... | 1 | 15 | 1365 | ,, | |
| 35 | 1.39 | 1 | 30 | 1355 | ,, | |
| 36 | ... | 0 | 48 | 1340 | ,, | Scull on top of hand-ladle. |
| 37 | ... | 0 | 47 | 1340 | ,, | |
| 38 | ... | 0 | 48 | 1340 | ,, | |
| 39 | 1.42 | 0 | 43 | 1330 | ,, | 12 minutes to cast 15 ingots. |
| 40 | ... | 0 | 48 | 1330 | ,, | |

TABLE I. (*continued*).

| Ingot No. | Time into Hand-ladle. | Time of Holding in Hand-ladle. | | Temperature of Pouring, Degrees C. | Condition of Metal. | Remarks. |
|---|---|---|---|---|---|---|
| | P. M. | Min. | Sec. | | | |
| 41 | ... | 0 | 45 | 1330 | Froze | |
| 42 | ... | 3 | 02 | 1330 | Hot | |
| 43 | Held in Mould | ... | | 1330 | Frozen | |
| 44 | ,, | ... | | 1330 | ,, | |
| 45 | ,, | ... | | 1330 | ,, | |
| 46 | ,, | ... | | 1330 | Hot | |
| 47 | ,, | ... | | 1330 | Cold | |
| 48 | ,, | ... | | 1330 | ,, | |
| 49 | 2.28 | 0 | 43 | 1330 | Hot | *Third Blow.*<br>Blown at 2-19-40.<br>Overblown at 2-20-04.<br>Down at 2-20-30.<br>Into ladle 2-22-30.<br>Scull removed 2-26-10.<br>Began pouring 2-27-40. |
| 50 | ... | 0 | 53 | 1340 | ,, | |
| 51 | 2.30 | 0 | 48 | 1335 | ,, | |
| 52 | ... | 0 | 44 | 1335 | ,, | |
| 53 | 2.32 | 0 | 43 | 1340 | Hot | |
| 54 | ... | 0 | 43 | 1330 | ,, | |
| 55 | 2.33 | 0 | 46 | 1335 | ,, | |
| 56 | ... | 0 | 45 | 1340 | ,, | |
| 57 | 2.34 | 0 | 47 | 1340 | Hot | Hand-ladle dropped. |
| 58 | ... | 1 | 14 | 1340 | ,, | |
| 59 | ... | 0 | 45 | 1340 | ,, | |
| 60 | ... | 0 | 48 | 1340 | ,, | |
| 61 | 2.39 | 0 | 47 | 1350 | Hot | 13 minutes to cast 15 ingots. |
| 62 | ... | 0 | 46 | 1350 | ,, | Spluttered in hand-ladle. |
| 63 | 2.41 | 2 | 5 | 1340 | ,, | Refilled after 1 min. 10 secs. |
| 64 | ... | 1 | 48 | 1340 | ,, | |
| 65 | ... | 0 | 44 | 1330 | Hot | |
| 66 | ... | 0 | 45 | 1330 | ,, | |
| 67 | ... | 0 | 43 | 1350 | ,, | |
| 68 | ... | 0 | 48 | 1350 | ,, | |
| 69 | Held in Mould | ... | | 1340 | Hot | |
| 70 | ,, | ... | | 1325 | Freezing | |
| 71 | ,, | ... | | 1340 | Hot | |
| 72 | ,, | ... | | 1340 | ,, | |

The temperatures were taken with a Holborn-Kurlbaum optical pyrometer by an experienced operator.

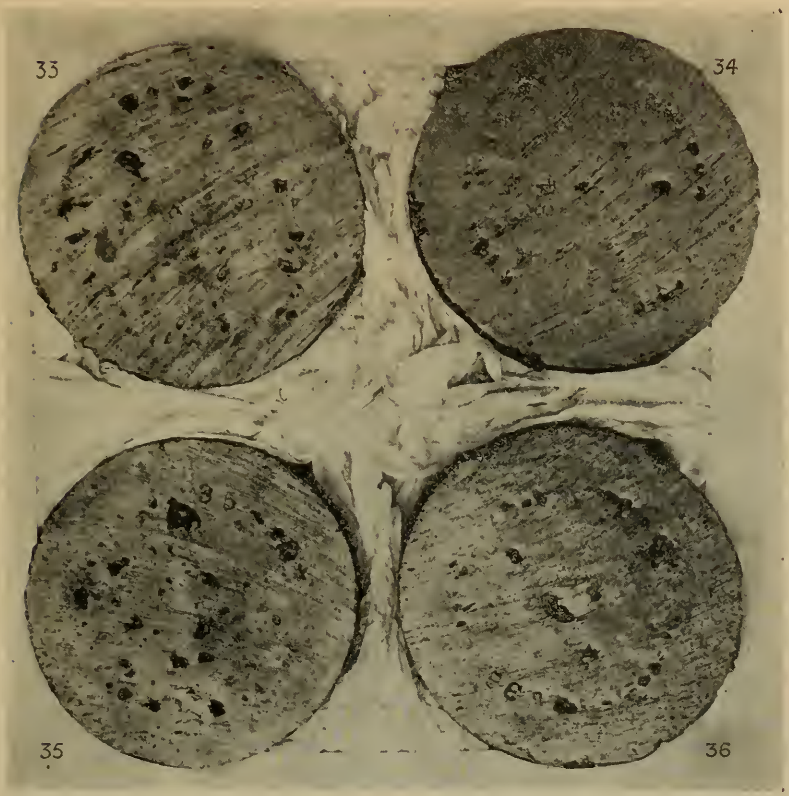

FIG. 13.

Ingots 33 and 34 with 0·05 per cent. Aluminium. Ingots 35 and 36 with 0·10 per cent. Aluminium. Transverse section at cropping point one-fourth actual size. Additions in ladle.

TABLE II.—*Chemical Analysis of Deoxidisers.*

| Deoxidiser. | Carbon per Cent. | Manganese per Cent. | Silicon per Cent. | Sulphur per Cent. | Phosphorus per Cent. | Aluminium per Cent. | Titanium per Cent. | Iron per Cent. |
|---|---|---|---|---|---|---|---|---|
| Ferro-manganese . . | 6·55 | 79·65 | 0·908 | 0·024 | 0·185 | ... | ... | ... |
| Ferro-silicon . . | 0·16 | ... | 56·0 | ... | ... | ... | ... | ... |
| Ferro-carbon titanium . | 5·92 | ... | 2·10 | ... | ... | None. | 14·32 | ... |
| Carbon-free ferro-titanium . . . | ... | ... | 1·30 | ... | ... | 7·61 | 24·0 | ... |
| Aluminium . . . | ... | ... | 0·87 | ... | ... | 99.08 by diff. | ... | 0·05 |

Table II. gives the chemical composition of the various deoxidisers used. Ferro-magnesium and ferro-vanadium were considered when planning the experiment, but the former is so expensive as to be limited to very high grade steels, and ferro-vanadium is also expensive and is not now advocated as a deoxidiser by the principal manufacturers, who state that, although ferro-vanadium has some deoxidising power, their instructions to users call for its addition under conditions where it cannot easily be oxidised, basing their claim to advantage on its effect on the physical properties, and making what is practically an alloy steel, although the proportions of vanadium used are generally very small. These two materials were therefore omitted.

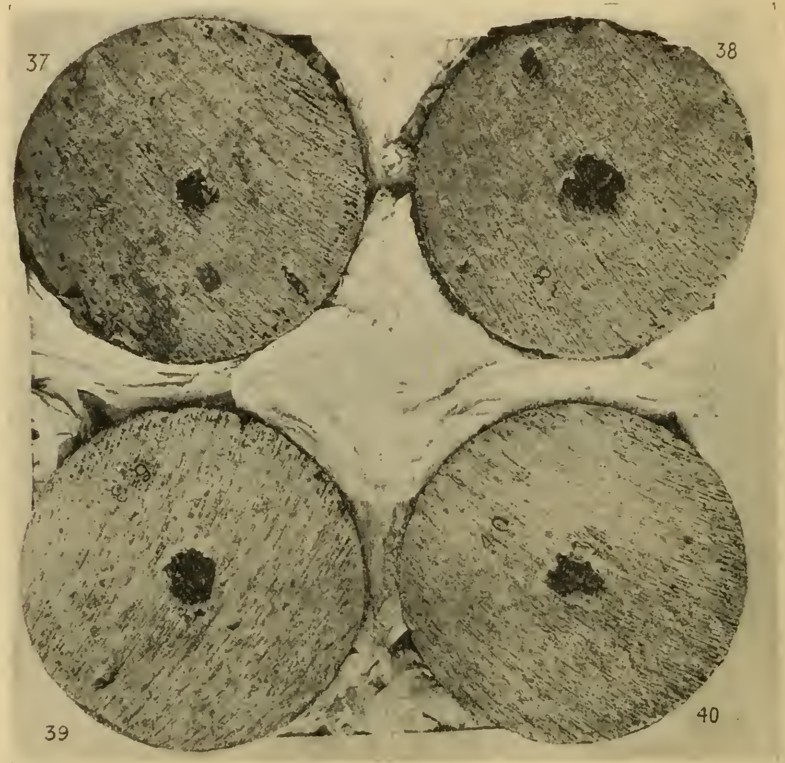

Fig. 14.

Ingots 37 and 38 with 0·20 per cent. Aluminium. Ingots 39 and 40 with 0·30 per cent. Aluminium. Transverse section at cropping point one-fourth actual size. Additions in ladle.

*Proportions of Deoxidisers Used.*—In Table III. are given the records of the various proportions of deoxidisers used. It will be noted that in the case of aluminium, additions were made in the mould in some cases as well as in the ladle.

## Table III.—*Heat A.*

| Ingot No. | Additions per Cent. | Additions in Form of | Weight of Deoxidiser. | | |
|---|---|---|---|---|---|
| | | | Ounces Calculated. | Ounces Weighed. | Ounces per Ton Calculated. |
| 1<br>2 | Titanium . 0·03 | 15 per cent, ferro-carbon titanium. | 5·4 | 5½ | 62·5 |
| 3<br>4 | ,, 0·045 | | 8·1 | 8 | 100 |
| 5<br>6 | ,, 0·06 | | 10·7 | 10½ | 131 |
| 7<br>8 | ,, 0·10 | | 17·9 | 18 | 225 |
| 9<br>10 | Titanium . 0·01 | 25 per cent. carbon-free ferro-titanium, pea size. | 1·1 | 1 | 12·5 |
| 11<br>12 | ,, 0·02 | | 2·2 | 2 | 25 |
| 13<br>14 | ,, 0·03 | | 3·2 | 3 | 37·5 |
| 15<br>16 | ,, 0·10 | | 10·7 | 10½ | 131 |
| 17<br>18 | Silicon . . 0·20 | 50 per cent. ferro-silicon. | 9·2 | 9 | 113 |
| 19<br>20 | ,, 0·30 | | 13·7 | 13½ | 169 |
| 21<br>22 | ,, 0·40 | | 18·3 | 18½ | 231 |
| 23<br>24 | ,, 0·50 | | 22·9 | 23 | 288 |
| *Heat B.* | | | | | |
| 25<br>26 | Manganese . 0·50 | 80 per cent. ferro-manganese. | 16·1 | 16 | 200 |
| 27<br>28 | ,, 0·75 | | 24·1 | 24 | 300 |
| 29<br>30 | ,, 1·00 | | 32·2 | 32 | 400 |
| 31<br>32 | ,, 1·25 | | 40·2 | 40 | 500 |

## TABLE III.—*Heat B* (*continued*).

| Ingot No. | Additions per Cent. | Additions in Form of | Weight of Deoxidiser. | | |
|---|---|---|---|---|---|
| | | | Ounces Calculated. | Ounces Weighed. | Ounces per Ton Calculated. |
| 33 | Aluminium . 0·05 | 94 – 98 per cent. granulated aluminium. | 1·3 | 1½ | 19 |
| 34 | | | | | |
| 35 | ,, 0·10 | | 2·6 | 2½ | 31 |
| 36 | | | | | |
| 37 | ,, 0·20 | | 5·2 | 5 | 63 |
| 38 | | | | | |
| 39 | ,, 0·30 | | 7·8 | 8 | 100 |
| 40 | | | | | |
| 41 | Aluminium . 0·05 | 94 – 98 per cent. granulated aluminium. | 1·3 | 1½ | 19 |
| 42 | | | | | |
| 43 | ,, 0·10 | | 2·6 | 2½ | 31 |
| 44 | | | | | |
| 45 | ,, 0·20 | | 5·2 | 5 | 63 |
| 46 | | | | | |
| 47 | ,, 0·30 | | 7·8 | 8 | 100 |
| 48 | | | | | |
| *Heat C.* | | | | | |
| 49 | Titanium . 0·03 | 15 per cent. ferro - carbon titanium. | 5·4 | 5½ | 62·5 |
| 50 | ,, 0·045 | | 8·1 | 8 | 100 |
| 51 | ,, 0·06 | | 10·7 | 10½ | 131 |
| 52 | ,, 0·10 | | 17·9 | 18 | 225 |
| 53 | Titanium . 0·01 | 25 per cent. carbon - free ferro - titanium, pea size. | 1·1 | 1 | 12·5 |
| 54 | ,, 0·02 | | 2·2 | 2 | 25 |
| 55 | ,, 0·03 | | 3·2 | 3 | 37·5 |
| 56 | ,, 0·10 | | 10·7 | 10½ | 131 |
| 57 | Silicon . . 0·20 | 50 per cent. ferro-silicon. | 9·2 | 9 | 113 |
| 58 | ,, 0·30 | | 13.7 | 13½ | 169 |
| 59 | ,, 0·40 | | 18·3 | 18½ | 231 |
| 60 | ,, 0·50 | | 22·9 | 23 | 288 |
| 61 | Manganese . 0·50 | 80 per cent. ferro - manganese. | 16·1 | 16 | 200 |
| 62 | ,, 0·75 | | 24·1 | 24 | 300 |
| 63 | ,, 1·00 | | 32·2 | 32 | 400 |
| 64 | ,, 1·25 | | 40·2 | 40 | 500 |

TABLE III.—*Heat C* (*continued*).

| Ingot No. | Additions per Cent. | Additions in Form of | Weight of Deoxidiser. | | |
|---|---|---|---|---|---|
| | | | Ounces Calculated. | Ounces Weighed. | Ounces per Ton Calculated. |
| 65 | Aluminium . 0·05 | 94 – 98 per cent. granulated aluminium. | 1·3 | 1½ | 19 |
| 66 | ,, 0·10 | | 2·6 | 2½ | 31 |
| 67 | ,, 0·20 | | 5·2 | 5 | 63 |
| 68 | ,, 0·30 | | 7·8 | 8 | 100 |
| 69 | Aluminium . 0·05 | 94 - 98 per cent. granulated alumium. | 1·3 | 1½ | 19 |
| 70 | ,, 0·10 | | 2·6 | 2½ | 31 |
| 71 | ,, 0·20 | | 5·2 | 5 | 63 |
| 72 | ,, 0·30 | | 7·8 | 8 | 100 |

In Column 2 are given the additions as calculated in percentages of the deoxidising element (titanium, aluminium, manganese, &c.). In Column 4 these percentages have been calculated in weights of the actual deoxidiser, using the chemical analyses given in Table II. ; while Column 5 gives the weights of deoxidiser actually used. The scales used in weighing were accurate to half an ounce. In the sixth column are given the weights of deoxidiser calculated in ounces per ton (from Column 5) for the sake of comparison with large scale experiments.

In Heats A and B it will be noted that there are duplicate ingots for each addition poured in succession. All additions were made in the hand-ladle except in the case of Ingots 41 to 48 inclusive and 69 to 72 inclusive (aluminium), where the additions were made in the mould. The hand-ladles and the ferro-manganese were preheated, the latter in a reducing flame to prevent premature oxidation. It was thought that if the ferro-manganese were not preheated it would tend to freeze the metal.

It should be borne in mind in interpreting the results of this experiment that ferro-carbon titanium contains about 2 per cent. of silicon, and carbon-free ferro-titanium about 1·3 per cent. silicon and 7·6 aluminium (see Table II.). The castings were divided into three heats, because of the mechanical difficulty of pouring more than 24 ingots from one heat (limited to about 5000 lbs. each). The arrangement of ingots was made to neutralise as far as possible any error due to difference in temperature or carbon content of the raw metal in the different heats.

*Chemical Analysis.*—The expense of making complete chemical analyses of all the ingots in Experiment 1 was prohibitive, but in Table IV. are shown analyses for carbon in Ingots 10, 41, and 53, these being representative ingots from those series in which the additions contained no carbon. In this table also are given the chemical analyses of representative ingots from Heat C showing the loss of deoxidising element in the respective cases. It is noteworthy that no titanium was found either in the case of ferro-carbon titanium or of carbonless ferro-titanium. The ingots analysed were chosen from those containing the proportions of deoxidiser giving the densest ingot and hence selected for Experiment 2.

TABLE IV.—*Chemical Analyses of Selected Ingots from Experiment* 1.

| Ingot No. | Approximate Percentage, Deoxidiser Added. | Heat No. | Carbon per Cent. | Manganese per Cent. | Silicon per Cent. | Titanium per Cent. | Aluminium per Cent. |
|---|---|---|---|---|---|---|---|
| 10 | 0·01 Ti | A | 0·030 | ... | ... | ... | ... |
| 41 | 0·05 Al | B | 0·043 | ... | ... | ... | ... |
| 53 | 0·01 Ti | C | 0·040 | ... | ... | ... | ... |
| 52 | 0·10 Ti as Fe-C Ti | C | 0·100 | ... | ... | None | ... |
| 56 | 0·10 Ti as Fe-Ti | C | 0·091 | ... | ... | None | ... |
| 59 | 0·40 Si | C | 0·081 | ... | 0·424<br>0·415 | ...<br>... | ...<br>... |
| 61 | 0·50 Mn | C | 0·114 | 0·40 | ... | ... | ... |
| 67 | 0·20 Al | C | 0·107 | 0·02 | 0·055 | ... | ... |

In both ingots where titanium was added it was all lost. In Ingot 61, where manganese was added, there was a loss of about 0·12 per cent. manganese, or about one-fourth of the manganese added, while in Ingot 59 there was a very slight loss of silicon, and in Ingot 67 about four-fifths of the aluminium was lost. It is difficult to explain why Ingots 56, 59, and 67 contain from twice to three times as much carbon as the raw converter metal. The small amount of carbon (0·16 per cent.) in the ferro-silicon is too small to account for the increase in carbon in this case. The manganese and silicon contents of Ingot 67 may be taken to represent those of raw metal in Heat C.

*Relative Density of Ingots in Experiment* 1.—The relative density of the ingots cast in Experiment 1, as determined by weighing in air and in water, was taken as the criterion for determining the proportion of each deoxidiser to be used in Experiment 2, where commercial steel was to be used.

The determinations are based on the assumption that each ingot will displace its own volume of water.

The ingots after being cropped were covered with shellaced paper to cover up the blowholes. The same treatment was given all the ingots irrespective of the extent of pipe or blowholes. The ingots were then weighed in air and in water, the weighings being made on a Howe platform scale sensitive to $\frac{1}{4}$ ounce. The accuracy of the scales was, however, about 1 ounce ±; this was determined by balancing different sets of weights on the scales.

A cylindrical tank with a tap at lower end was used, and water was drawn off from the service pipe 24 hours in advance

*Erratum.*

*Page* 122. In Table IV., 0·028 per cent. should appear for Ingot 67 in the column headed "Aluminium."

and allowed to stand to free it from air and to allow the temperature to become constant. The tank was insulated to prevent change of temperature of the water by radiation. The water was always brought to the same level by means of a suitable gauge.

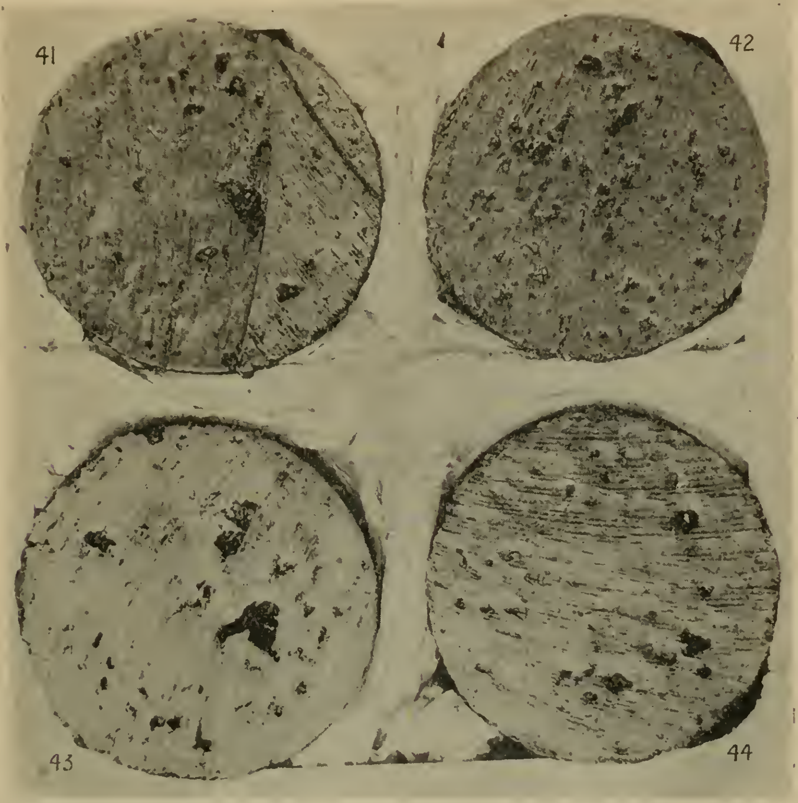

FIG. 15.

Ingots 41 and 42 with 0·05 per cent. Aluminium. Ingots 43 and 44 with 0·10 per cent. Aluminium. Transverse section at cropping point one-fourth actual size. Addition in mould.

*Formula for the Relative Density.*—The derivation of the formula for relative density is as follows. The letters are those used in Table V.

T = weight of empty tank = 27·22 lbs.
Oct. 23. W1 = weight of tank + water up to mark = 106·66 lbs.
,, 24. W1 = 106·75 lbs.
,, 27. W1 = 106·84 lbs.
Nov. 3. W1 = 106·61 lbs.
,, 3. W1 = 106·60 lbs.
W2 = weight of tank + water to bring up to mark, with ingot in tank.
I = weight of ingot in air.
W2 + I = weight of tank + water to mark + ingot.
W1 − W2 = W3 = weight of water displaced by ingot.

The volume of W3 is assumed as equal to the volume of the ingot. The same water was used for all weighings and, since relative density rather than the precise specific gravity was sought, the specific gravity of the water was not determined. The difference in temperature of the water proved to be a negligible factor, the temperature varying not more than 5° C. at a temperature of about 20° C. In the worst case the error amounted to only 0·1 per cent. of the weight of water displaced by the ingot, this being equal to about 0·01 lb., or about $\frac{1}{6}$ of the maximum error possible in weighing.

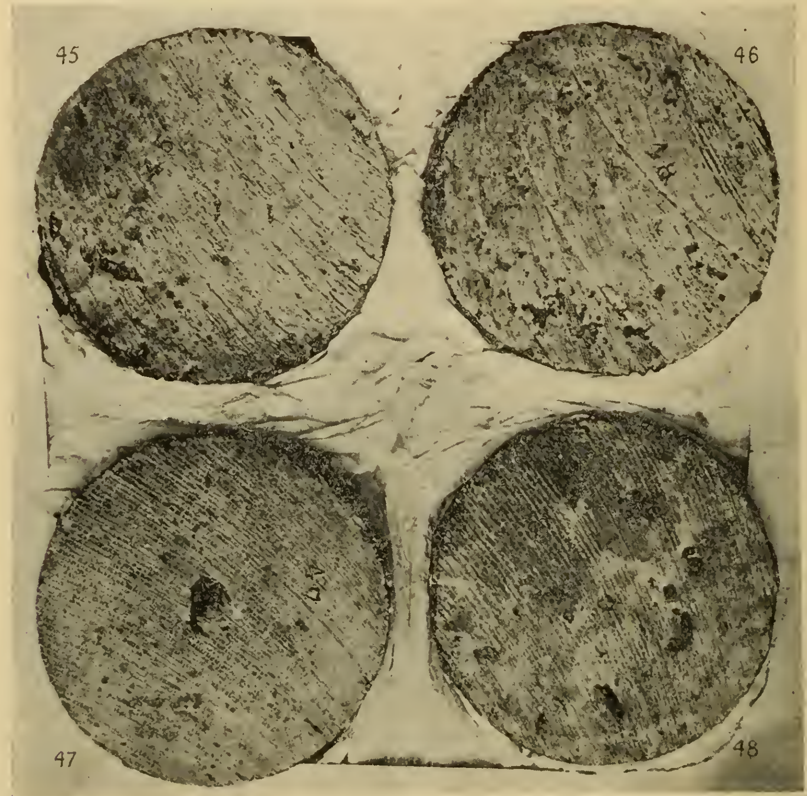

Fig. 16.

Ingots 45 and 46 with 0·20 per cent Aluminium. Ingots 47 and 48 with 0·30 per cent. Aluminium. Transverse section at cropping point one-fourth actual size. Additions in mould.

$$\frac{I}{W3} = \text{relative density of ingot.}$$

Table V. gives the weights of the ingots with their relative densities, the proportions of deoxidisers used, and the average relative density of the three ingots containing like proportions of the same deoxidiser.

TABLE V.—*Density of Ingots in Experiment* 1.

| Ingot No. | Addition. | Heat No. | Weight of Ingots, Lbs. | Relative Density. | Average Relative Density. | Condition of Metal. |
|---|---|---|---|---|---|---|
| 1 | 0·03 per cent. titanium-carbon | A | 95·94 | 5·815 | 6·510 | ... |
| 2 | | A | 104·25 | 6·632 | | ... |
| 49 | | C | 98·44 | 6·388 | | ... |
| 3 | 0·045 per cent. titanium-carbon | A | 104·84 | 6·848 | 6·674 | ... |
| 4 | | A | 98·31 | 6·355 | | ... |
| 50 | | C | 104·11 | 6·813 | | ... |
| 5 | 0·06 per cent. titanium-carbon | A | 101·13 | 6·619 | 6·823 | Freezing |
| 6 | | A | 101·38 | 6·609 | | Freezing |
| 51 | | C | 110·19 | 7·241 | | ... |
| 7 | 0·10 per cent. titanium-carbon | A | 105·56 | 6·690 | 6·823 | ... |
| 8 | | A | 101·50 | 6·599 | | ... |
| 52 | | C | 114·92 | 7·152 | | ... |
| 9 | 0·01 per cent. titanium | A | 95·75 | 6·154 | 6·229 | Cold |
| 10 | | A | 93·88 | 6·069 | | ... |
| 53 | | C | 100·06 | 6·464 | | ... |
| 11 | 0·02 per cent. titanium | A | 101·25 | 6·340 | 6·387 | ... |
| 12 | | A | 94·00 | 5·980 | | ... |
| 54 | | C | 104·08 | 6·925 | | ... |
| 13 | 0·03 per cent. titanium | A | 98·79 | 6·205 | 6·235 | ... |
| 14 | | A | 99·97 | 6·372 | | ... |
| 55 | | C | 101·00 | 6·129 | | ... |
| 15 | 0·10 per cent. titanium | A | 115·38 | 7·444 | 7·287 | Froze |
| 16 | | A | 113·41 | 7·031 | | Froze |
| 56 | | C | 113·81 | 7·424 | | ... |
| 17 | 0·20 per cent. silicon | A | 113·63 | 7·213 | 7·348 | ... |
| 18 | | A | 103·44 | 7·341 | | Cold |
| 57 | | C | 77·31 | 7·770 | | Ladle dropped |
| 19 | 0·30 per cent. silicon | A | 90·38 | 7·173 | 7·637 | ... |
| 20 | | A | 124·50 | 7·950 | | ... |
| 58 | | C | 116·72 | 7·787 | | ... |
| 21 | 0·40 per cent. silicon | A | 114·03 | 7·700 | 7·838 | ... |
| 22 | | A | 119·50 | 7·821 | | ... |
| 59 | | C | 120·36 | 7·993 | | ... |
| 23 | 0·50 per cent. silicon | A | 69·75 | 7·75 | 7·77 | Cold |
| 24 | | A | ... | ... | | ... |
| 60 | | C | 114·44 | 7·79 | | ... |
| 25 | 0·50 per cent. manganese | B | 88·25 | 7·077 | 7·145 | ... |
| 26 | | B | 115·59 | 7·144 | | ... |
| 61 | | C | 99·06 | 7·215 | | ... |
| 27 | 0·75 per cent. manganese | B | 112·38 | 7·208 | 6·950 | ... |
| 28 | | B | 112·88 | 6·934 | | ... |
| 62 | | C | 84·59 | 6·682 | | ... |

TABLE V.—*continued.*

| Ingot No. | Addition. | Heat No. | Weight of Ingots, Lbs. | Relative Density. | Average Relative Density. | Condition of Metal. |
|---|---|---|---|---|---|---|
| 29 | 1·00 per cent. manganese | B | 105·94 | 6·875 | 6·839 | ... |
| 30 | | B | 110·78 | 6·924 | | ... |
| 63 | | C | 78·34 | 6·719 | | ... |
| 31 | 1·25 per cent. manganese | B | 72·88 | 6·961 | 6·971 | ... |
| 32 | | B | 95·97 | 7·026 | | Spilled |
| 64 | | C | 81·38 | 6·926 | | ... |
| 33 | 0·05 per cent. aluminium | B | 103·5 | 6·774 | 6·963 | ... |
| 34 | | B | 113·88 | 6·914 | | ... |
| 65 | | C | 95·98 | 7·200 | | ... |
| 35 | 0·10 per cent. aluminium | B | 96·55 | 6·724 | 6·678 | ... |
| 36 | | B | 106·38 | 6·903 | | Scull on ladle |
| 66 | | C | 74·06 | 6·346 | | ... |
| 37 | 0·20 per cent. aluminium | B | 119·69 | 7·979 | 7·935 | ... |
| 38 | | B | 123·08 | 7·915 | | ... |
| 67 | | C | 97·38 | 7·912 | | Sputtered in ladle |
| 39 | 0·30 per cent. aluminium | B | 118·08 | 7·784 | 7·824 | ... |
| 40 | | B | 116·81 | 7·715 | | ... |
| 68 | | C | 104·25 | 8·644 | | ... |
| 41 | 0·05 per cent. aluminium | B | 87·66 | 6·417 | 6·989 | Froze |
| 42 | | B | 54·75 | 7·242 | | Hot; refilled |
| 69 | | C | 82·88 | 7·309 | | ... |
| 43 | 0·10 per cent. aluminium | B | 86·78 | 6·645 | 7·118 | Froze |
| 44 | | B | 79·31 | 6·951 | | Froze |
| 70 | | C | 86·03 | 7·757 | | Freezing |
| 45 | 0·20 per cent. aluminium | B | 85·34 | 6·364 | 6·806 | Froze |
| 46 | | B | 62·28 | 6·023 | | ... |
| 71 | | C | 102·16 | 8·031 | | ... |
| 72 | 0·30 per cent. aluminium | B | 113·12 | 7·727 | 7·441 | Cold |
| 48 | | B | 69·72 | 7·324 | | Cold |
| 72 | | C | 98·19 | 7·273 | | ... |

A curious relation exists between the weight of the ingot and the relative density. In almost every case the greater the weight the greater the relative density. The reason for the variation in the weight (which was intended to be 120 lbs. in every case after cropping) is that some of the metal stuck in the hand-ladles and could not be poured. The smallest ingot was No. 42, weighing 54·75 lbs. (cropped). The heaviest ingot was No. 20, and it weighed 124·50 lbs. (cropped).

The density of ingot No. 1 was ignored in the average because of a large cavity in the top of the ingot.

*Results.*—It will be seen that in the majority of cases the relative densities are as constant as could be expected with the variation in pouring temperature, which could not be entirely avoided.

On the following chart are plotted the average relative densities. It will be noted that for the proportions used aluminium added in the ladle gives the densest ingots in general, while the general efficacy of the other deoxidisers is in the following order:

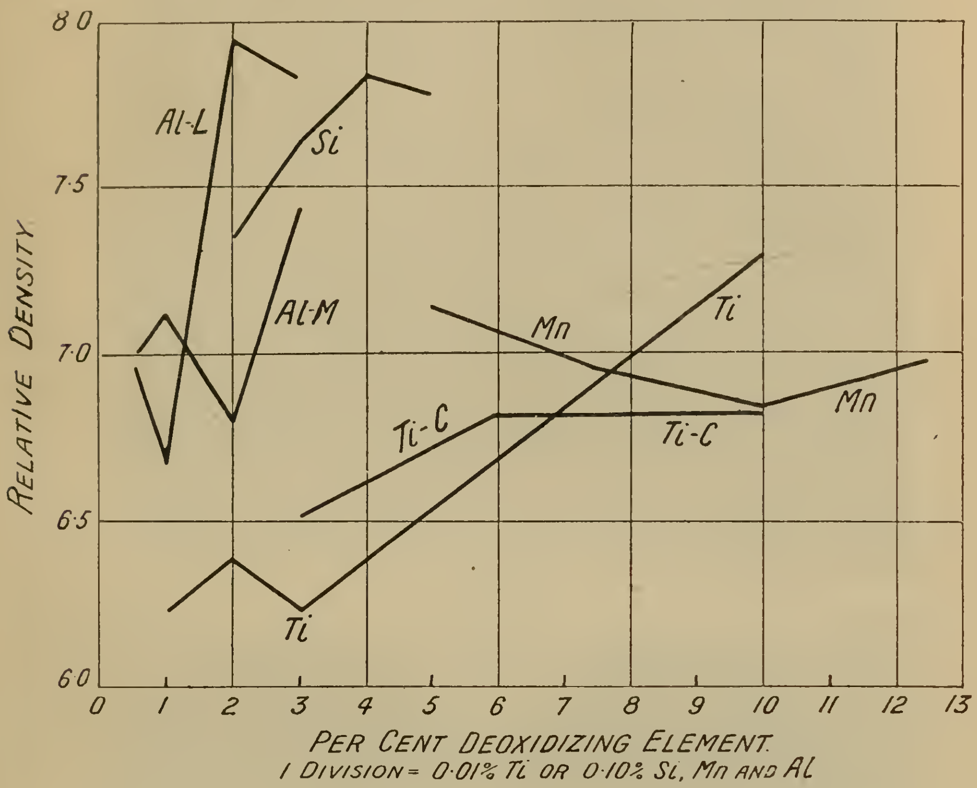

FIG. 17.—Diagram showing Relative Density of Ingots of Converter Metal with various Deoxidisers added.

Al-L = Aluminium added in ladle.
Al-M = Aluminium added in mould.
Si = Ferro-silicon.
Ti = Carbon-free ferro-titanium.
Ti-C = Ferro-carbon titanium.
Mn = Ferro-manganese.

Silicon.
Aluminium in the mould.
Carbon-free ferro-titanium.
Ferro-manganese.
Ferro-carbon titanium.

The curves cross each other somewhat, but the maximum of each curve is taken as the criterion. It will be noted that

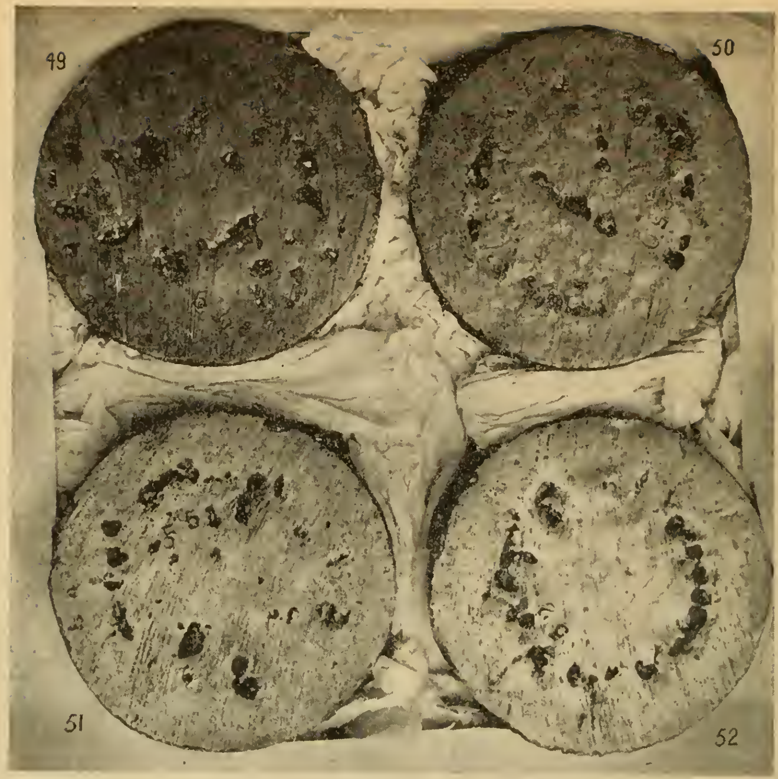

FIG. 18.

Ingots 49 to 52 with 0·03, 0·045, 0·06, and 0·10 per cent. Titanium in form of 15 per cent. ferro-carbon titanium. Transverse section at cropping point one-fourth actual size.

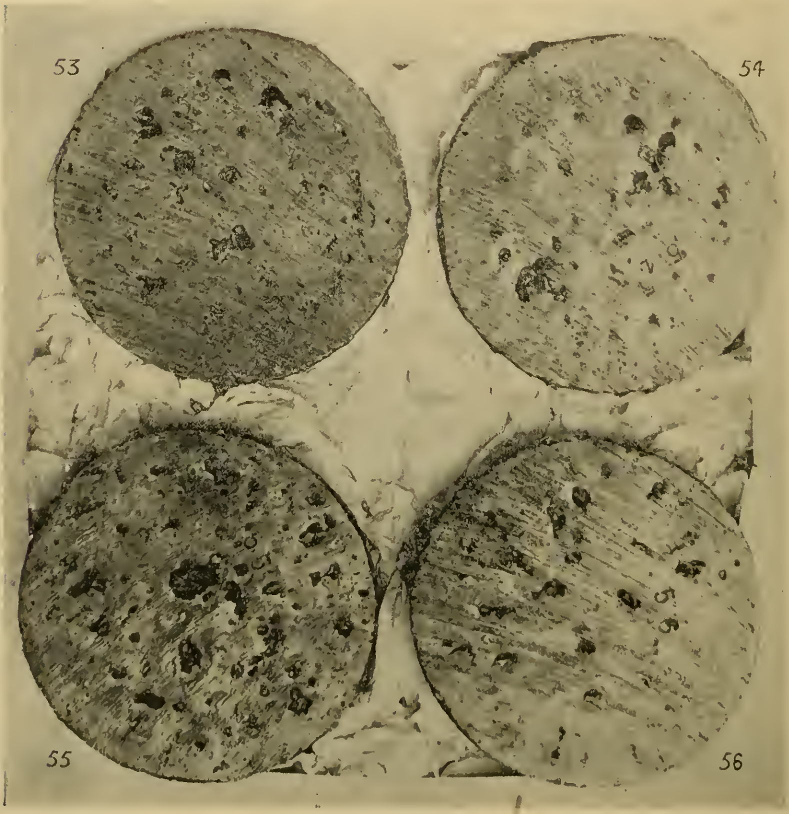

FIG. 19.

Ingots 53 to 56 with 0·01, 0·02, 0·03, and 0·10 per cent. Titanium respectively in form of 25 per cent. carbon-free ferro-titanium. Transverse section at cropping point one-fourth actual size.

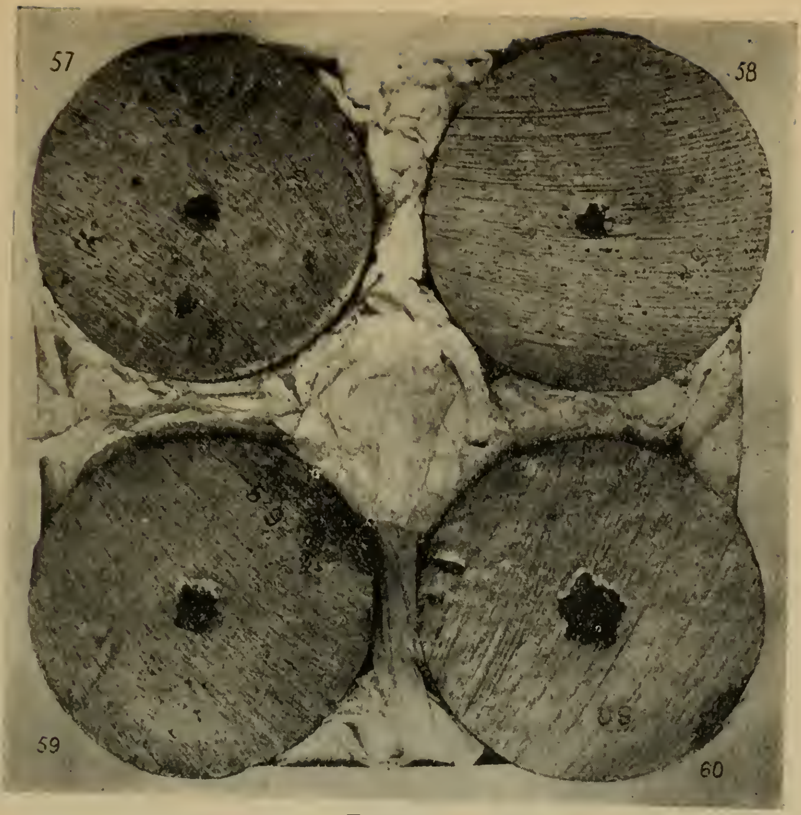

FIG. 20.

Ingots 57 to 60 with 0·20, 0·30, 0·40, and 0·50 per cent. Silicon respectively in form of 50 per cent. ferro-silicon. Transverse section at cropping point one-fourth actual size.

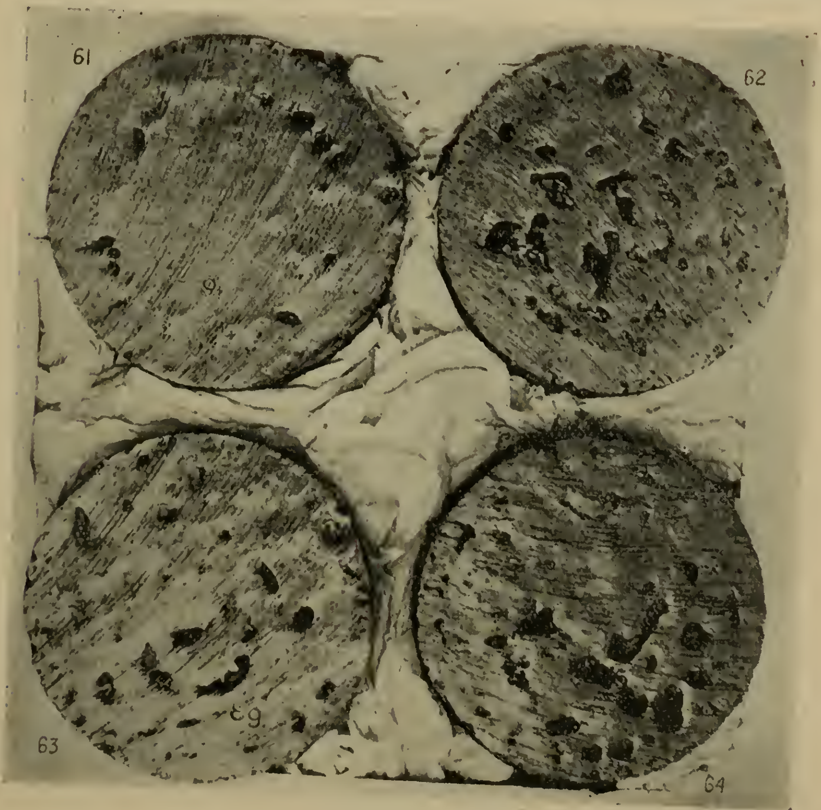

FIG. 21.

Ingots 61 to 64 with 0·50, 0·75, 1·00, and 1·25 per cent. Manganese respectively as 80 per cent. ferro-manganese. Transverse section at cropping point one-fourth actual size.

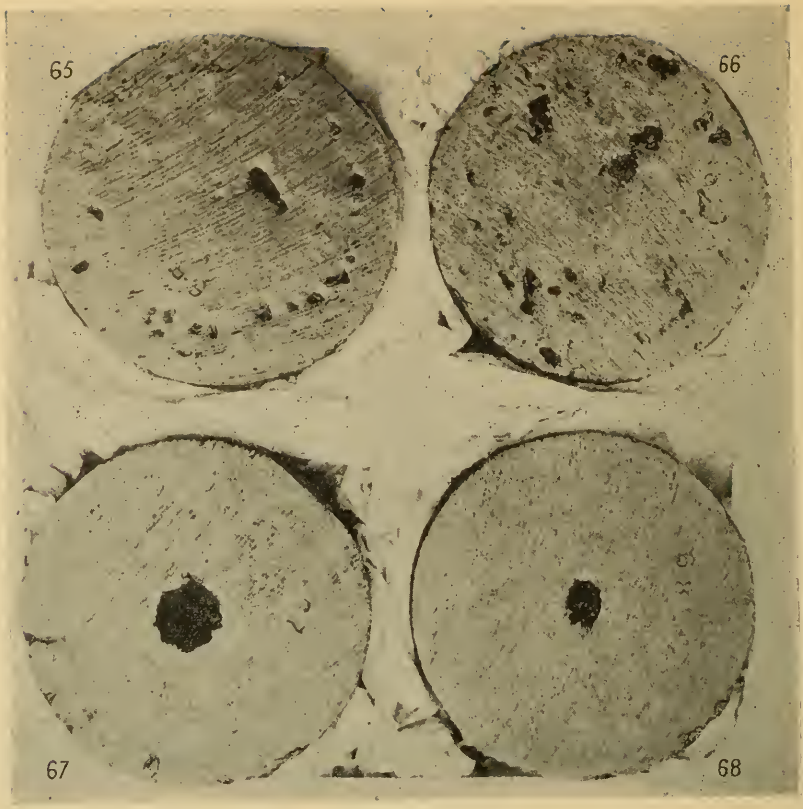

FIG. 22.

Ingots 65 to 68 with 0·05, 0·10, 0·20, and 0·30 per cent. Aluminium respectively added in ladle. Transverse section at cropping point one-fourth actual size.

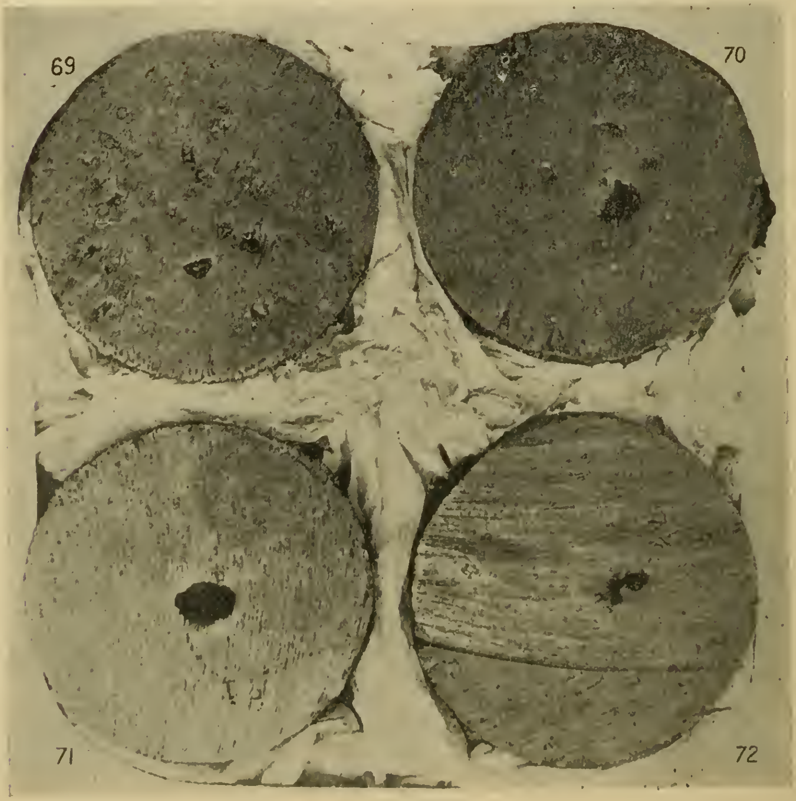

FIG. 23.

Ingots 69 to 72 with 0·05, 0·10, 0·20, and 0·30 per cent. Aluminium respectively, added in mould. Transverse section at cropping point one-fourth actual size.

the smallest proportion of ferro-manganese gives the best results, further additions apparently chilling the metal. The curve for ferro-manganese begins to rise again, however, for the highest proportion used, and this is a point that will bear further investigation.

The scale of relative densities has purposely been exaggerated to bring out more clearly the difference in relative density.

## PHOTOGRAPHS.

Photographs of the cross sections of the cropped ingots were taken at the point of cropping, and the results are shown in Figs. 5 to 23. In general they were very consistent with the relative density figures. It will be noted that in most cases aluminium and silicon produce a small pipe but few if any blowholes, whereas both titanium alloys and ferro-manganese produce many blowholes, but little, if any, pipe.

The object of Experiment 1 was principally to determine the proportion of deoxidiser to be used in Experiment 2, and too much value must not be attached to the comparison of the various deoxidisers based on this experiment, for it must be remembered that the material used was raw converter metal and not commercial steel, and no physical tests (except density) were made. Nevertheless the conclusion is inevitable that apart from other additions, and considering the proportions of deoxidiser used, aluminium and silicon are notably better agents than the other for increasing the density of blown metal and almost equally effective when the proper proportions are used, the preference inclining slightly in favour of aluminium (in the ladle). Moreover, the slight porosity of the metal to which these two deoxidisers have been added is due to a slight pipe rather than to blowholes.

Further experiments are in course of being undertaken.

# INVESTIGATION OF THE RELATIVE MERITS OF VARIOUS AGENTS FOR THE DEOXIDATION OF STEEL.

By H. M. BOYLSTON (Cambridge, U.S.A.).

## PART II.

In Part I. of this report already published (see p. 102) the author described the results of adding various deoxidising agents in different proportions to raw converter metal. The present report includes the description of a similar experiment with the exception that in this case steel with about 0·50 per cent. carbon was used instead of converter metal, and only one proportion of deoxidiser was used in each case, namely, the proportion found by Experiment 1[1] to give the soundest ingot when added to raw converter metal.

The proportions of deoxidising element aimed at in Experiment 2 were as follows:

| | Per Cent. |
|---|---|
| Titanium (Fe.C.Ti.) . . . . | 0·1 |
| Manganese (Fe.Mn.) . . . . | 0·5 |
| Titanium (Fe.Ti.) . . . . . | 0·1 |
| Silicon (Fe.Si.) . . . . . | 0·4 |
| Aluminium (Al.) . . . . . | 0·2 |

The same stock of deoxidising material was used in Experiment 2 in each case as was used in Experiment 1, and the deoxidisers were: 15 per cent. ferro-carbon-titanium, designated in the following tables as Fe.C.Ti., 80 per cent. ferro-manganese (Fe.Mn.), 25 per cent. carbon-free ferro-titanium (Fe.Ti.), 56 per cent. ferro-silicon (Fe.Si.), and commercially pure aluminium (Al.). The proportions of deoxidiser actually added will be found in Table III., and all additions were very close to those aimed at, with the exception of aluminium, where more steel was used than was planned, bringing the percentage of aluminium down to 0·144. The results as reported here are known as Experiment 2, and very complete physical and some chemical tests were made on all the ingots.

---

[1] *Carnegie Scholarship Memoirs*, 1915, vol. vii. Part I. Fig. 17, p. 127.

### Experiment 2.

*Material Used.*—One heat of metal from a Tropenas converter was used, the aim being to obtain steel of the following composition :

| | Per Cent. |
|---|---|
| Carbon . . . . . . . | 0·40 |
| Manganese . . . . . . | 0·50 |
| Silicon . . . . . . . | 0·20 |
| Phosphorus . . . . . . | 0·05 |
| Sulphur . . . . . . . | 0·05 |

Cupola metal of the same analysis as used for the heat of steel was added as a recarburiser (see chemical analysis in Table II.). Enough ferro-manganese and ferro-silicon of the analysis given in Table II. were used to bring the manganese and silicon content up to the requirements. The various deoxidisers under test were then added in the proportion (determined in Experiment 1) which gave the soundest ingots when added to raw converter metal.

*Procedure.*—Steel was made in the usual way by blowing cupola iron in the Tropenas converter, adding to it the required amount of cupola metal for recarburising, and teeming the mixture into a preheated 2-ton ladle in which had been weighed the correct proportions of ferro-manganese and ferro-silicon to give the analysis desired. The record of the heat is given in Table I.

Table I.—*Experiment* 2. *Details of Heat.*

| Heat No. 4458. | Weight, lbs. | Time. |
|---|---|---|
| Metal into converter . . . . . | ... | 2·09<br>2·12 |
| Weight of metal into converter . . | 6020 | ... |
| Started to blow . . . . . . | ... | H. M. S.<br>2 12 30 |
| Blow ended . . . . . . . | 7 seconds over-blown. | H. M. S.<br>2 48 40 |
| Weight of cupola metal added to converter metal . . . . . . . | 425 | ... |
| Weight of empty 2-ton ladle . . . . | 3061 | ... |
| Weight of Fe.Mn. added (77·00 per cent. Mn.) | 45 | ... |
| Weight of Fe.Si. added (56 per cent. Si.) . | 7 | ... |
| Converter to 2-ton ladle . . . . . | ... | H. M. S.<br>3 00 00 |
| Weight of converter metal added . . | 5092 | ... |
| Weight of steel + additions . . . | 5569 | ... |

In Table II. are given chemical analyses of the raw materials and of the steel before the deoxidising additions were made. A comparison of the figures for the calculated analysis with the actual analysis of the steel will show the losses of carbon, manganese, and silicon by combination with the oxides in the overblown steel. Again, as in Experiment 1, 0·17 per cent. or one-fourth of the manganese and a small amount of the silicon have been lost.

TABLE II.—*Experiment 2. Chemical Analysis of Raw Material and Steel.*

| Analysis. | C. | Mn. | Si. | S. | P. |
|---|---|---|---|---|---|
| Cupola iron . . . . | 3·40 | 0·47 | 1·65 | 0·047 | 0·035 |
| Converter metal . . . | 0·082 | trace | 0·016 | ... | ... |
| Converter metal + additions by calculation . . . . | 0·387 | 0·68 | 0·218 | 0·0537 | 0·04001 |
| Same. By analysis . . . | 0·37 | 0·51 | 0·186 | 0·057 | 0·037 |
| Ferro-manganese . . . | 6·55 | 77·00 | 0·908 | 0·024 | 0·185 |
| Ferro-silicon . . . . | 0·16 | ... | 56·0 | ... | ... |

The metal in the 2-ton ladle was carried to preheated ladles, each of the capacity of 1000 lbs., three of these ladles being used. These 1000-lb. ladles had been weighed, and approximately 1000 lbs. of metal was teemed into each, and weighed.

The first and second 1000-lb. ladles were used for the fourth and fifth sets of deoxidisers.

The arrangement of moulds was approximately as shown in the sketch (Fig. 1) in order to facilitate quick pouring.

*Number of Ingots.*—Fifteen ingots in all were poured, three with each addition. All the deoxidising additions were made in the ladle, since it was determined from Experiment 1 that aluminium added in the mould did not give as good results as aluminium added in the ladle.

In addition to the above there was cast a small ingot of raw converter metal (Ingot 17), and one of converter metal to which the carbon, manganese, and silicon additions had been made, but to which no deoxidiser considered as such had been added (Ingot 18). Ingots 4 and 10 were small because there was not enough metal left in the 1000-lb. ladle to fill the mould. These two ingots were, therefore, not tested.

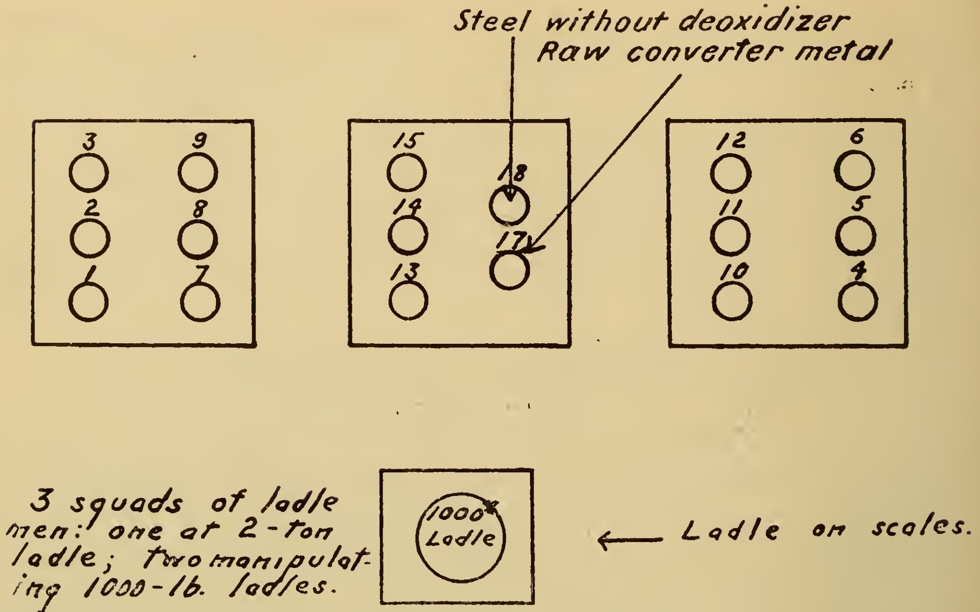
Steel without deoxidizer
Raw converter metal
3
9
2
8
1
7
15
18
14
17
13
12
6
11
5
10
4
1000 Ladle
3 squads of ladle men: one at 2-ton ladle; two manipulating 1000-lb. ladles.
Ladle on scales.

FIG. 1.—Arrangement of Moulds.

TABLE III.—*Experiment 2. Time of Pouring and Amount of Deoxidiser.*

| Ingot No. | 1–2–3. | 6–5–4. | 7–8–9. | 12–11–10. | 13–14–15. |
|---|---|---|---|---|---|
| | H. M. S. | H. M. S. | H. M. S. | H. M. S. | H. M. S. |
| Metal into ladle | 3 5 50 | 3 16 55 | 3 7 30 | 3 14 48 | 3 8 55 |
| Deoxidiser added | 3 5 56 | 3 16 56 | 3 7 30 | 3 14 48 | 3 9 00 |
| Finished pouring into ladle | 3 6 25 | 3 17 00 | 3 7 57 | 3 15 10 | 3 9 05 |
| Metal poured into first ingot | 3 09 20 | 3 19 45 | 3 10 25 | 3 17 14 | 3 11 35 |
| Third ingot finished | 3 10 56 | 3 21 20 | 3 11 34 | 3 18 31 | 3 13 00 |
| Deoxidiser held in ladle | 0 2 55 | 0 2 45 | 0 2 28 | 0 2 04 | 0 2 30 |
| Weight of deoxidiser added, lbs. | 6·98 | 6·275 | 4·16 | 7·15 | 2·02 |
| Weight of steel to which added, lbs. | 1054 | 1015 | 1067 | 1000 ? [1] | 1395 |
| Per cent. deoxidising element added | 0·095 | 0·492 | 0·0937 | 0·40 | 0·144 |
| Kind of deoxidiser added | Fe.C.Ti. | Fe.Mn. | Fe.Ti.<br>carbon-free | Fe.Si. | Al. |
| Per cent. of element in deoxidiser | 14·32 | 79·65 | 24·0 | 56 | 99·08 |
| Ounces of deoxidiser (calculated) per ton of steel | 212 | 198 | 125 | 229 | 46 |
| Ounces of deoxidising element (calculated) per ton of steel | 30·4 | 157·7 | 30·0 | 128 | 45·6 |

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[1] This weight was estimated as the scales were temporarily unmanageable. There were at least 1000 lbs. in the ladle, however.

Table III. gives the time of pouring, the weight and percentage of deoxidiser added, kind of deoxidiser, &c.

*Time of Holding.*—The deoxidised metal was held from two minutes to three minutes in the ladle before pouring into the moulds.

*Homogeneity of Metal.*—All ingots were cast from one heat, and manganese and silicon additions were added to the entire bulk of steel, so that the steel was as homogeneous as possible. Each 1000-lb. ladle gave enough metal for three ingots and the deoxidiser was added in these ladles, so that the homogeneity of the steel with any given deoxidising addition was also as homogeneous as possible. The deoxidiser was added to the 1000-lb. ladle while the steel was being poured into it, the first portion of deoxidiser going in when the ladle was about half full, and the additions being completed just before the last portion of steel was poured from the 2-ton ladle. This allowed a thorough mixing of the deoxidiser with the metal.

*Size of Ingots.*—Ingots were made as large as possible, keeping in mind that one heat of metal was to be used for the entire set. The pattern for the mould was made about 25 inches long and 7¼ by 7¾ inches in diameter at the respective ends, the mould being slightly tapered for draft, with the larger end up. The ingots weighed from 179 to 222 lbs. each, with the exception of Ingots 4 and 10, which were discarded. Ingots 17 and 18 were intended to be the same size as the others, but there was not enough metal left.

*Splitting and Photography of Ingots.*—All the ingots were sand-blasted, and all but Ingots 4, 10, 17, and 18 were cropped to 20 per cent. of their length. Ingots 4 and 10 were discarded, and 17 and 18 were very small and therefore were not cropped. Each ingot was then split vertically, and five representative ingots (Nos. 2, 5, 8, 11, and 14) were etched with a saturated solution of iodine in 95 per cent. alcohol to bring out differences in the microscopic structure due to segregation. All of the ingots were then photographed (see Plates XII. to XVII.).

*Piping.*—No special precautions were taken to prevent piping by mechanical means. This was intentional, as, at the time the plans were made, it was thought better not to confuse the effect of mechanical and chemical methods on the formation of pipe, since the prevention of piping as such was not to be studied. It is now believed that it would have been better to reduce or eliminate the pipe by mechanical means, as any effect of the chemical additions (deoxidisers) on the piping would thus have been more clearly shown. As a matter of fact all of the ingots were piped more or less for a considerable distance below the point of cropping. The value of the different deoxidisers as given in terms of the pipe in these cropped ingots would be: Ferro-carbon-titanium; ferro-silicon; aluminium; ferro-manganese; carbon-free ferro-titanium. The hidden pipe in Ingot 8 (carbon-free ferro-titanium) is especially noticeable. No evidence of this pipe was visible on the transverse section at the cropping point.

*Blowholes* are plainly visible in Ingots 3 (ferro-carbon titanium) and 5 and 6 (ferro-manganese). Ingot 5 (ferro-manganese) also has a hidden pipe.

TABLE IV.—*Relative Density Tests.*[1]

| Ingot No. | Weight of Ingot. | Relative Density. | Average Density. | Deoxidiser Used. | Order of Deoxidiser in respect to Density. |
|---|---|---|---|---|---|
| 1 | 220·45 | 7·87 | 7·85 | Fe.C.Ti. | 1 |
| 2 | 222·41 | 7·94 | | | |
| 3 | 218·08 | 7·75 | | | |
| 5 | 179·13 | 7·68 | 7·76 | Fe.Mn. | 5 |
| 6 | 195·11 | 7·84 | | | |
| 7 | 220·20 | 7·86 | 7·82 | Fe.Ti. carbon-free | |
| 8 | 222·58 | 7·82 | | | |
| 9 | 216·16 | 7·78 | | | |
| 11 | 219·23 | 7·71 | 7·77 | Fe.Si. | 4 |
| 12 | 219·64 | 7·83 | | | |
| 13 | 205·32 | 7·82 | 7·79 | Al. | 3 |
| 14 | 211·08 | 7·75 | | | |
| 15 | 218·20 | 7·81 | | | |

---

[1] It will be noted that the average relative densities are very close to each other, especially in the cases of ferro-manganese, ferro-silicon, and aluminium. In any particular group using the same deoxidiser, however, the relative densities vary more than the averages of the different groups. These variations are probably due to differences in casting conditions, and it was to eliminate such influences as far as possible that the ingots were cast in triplicate. The same remarks refer to the specific gravity tests on the small specimens given in Table V.

*Density.*—The half-ingots which were photographed were split in two transversely, and the lower ends were reserved for relative density tests.

Relative density tests were also made on the cropped ingots before splitting vertically, using the same method as in Experiment 1. The result of this test is given in Table IV., but no valuable conclusions can be drawn because no attempt was made to distinguish between the porosity due to blowholes and the porosity due to piping.

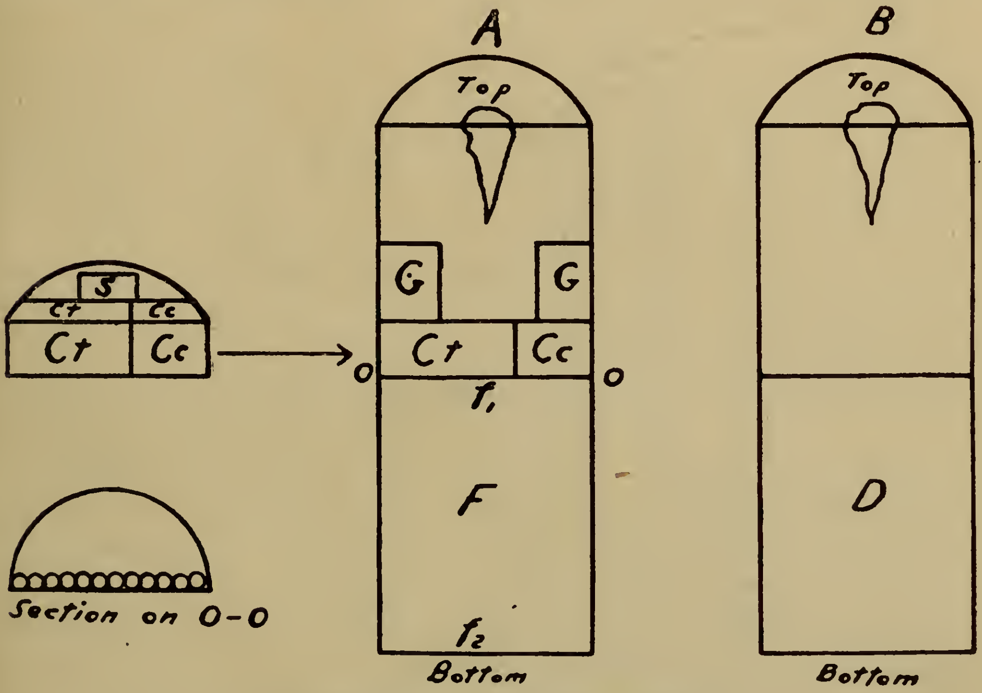

FIG. 8.—Position of Test-bars in Ingots.

Figs. 8 and 9 show the manner in which the cropped ingots were cut up for the various tests. Pieces located at GG in half-ingot A have been reserved for gas extraction tests. A 2-inch slice was cut out at the location C*t* and C*c* and a bar about 2 inches square was cut from this slice, the portion C*t* being machined for tensile test-bars (see Tables VI.–IX.), the portion C*c* for Charpy test-bars (see Tables X. and XI.), and pieces shown at S for specific gravity tests referred to in Table V. The section on O-O shows the location on the lower half of this half-ingot of the samples for oxide determination.

The lower half of this half-ingot marked F was forged as shown in Fig. 9, and tensile and Charpy tests were taken as shown in that sketch.

The lower half of the half-ingot B (marked D) has been reserved for density tests.

The half-ingot B was also used for determining segregation by chemical analysis, etching tests, and photography.

*Specific Gravity Tests* were made on small specimens weighing about 50 grammes, and taken from the point S indicated in the sketch above (Fig. 8). These are not considered of much value, as one large blowhole in any specimen might vitiate the results, as is evidently the case in Ingot 6. The results are given for what they are worth, however, and it is interesting to note the general agreement between the results of this test and the results of the relative density test given in Table IV. It is believed, however, that the relative density tests on the quarter-ingots reserved as indicated above will be more valuable than those given in either Table IV. or V., as the samples are much more representative, bearing in mind that the purpose of these tests is to show the relative freedom from blowholes and non-metallic inclusions, both of which would affect the density.

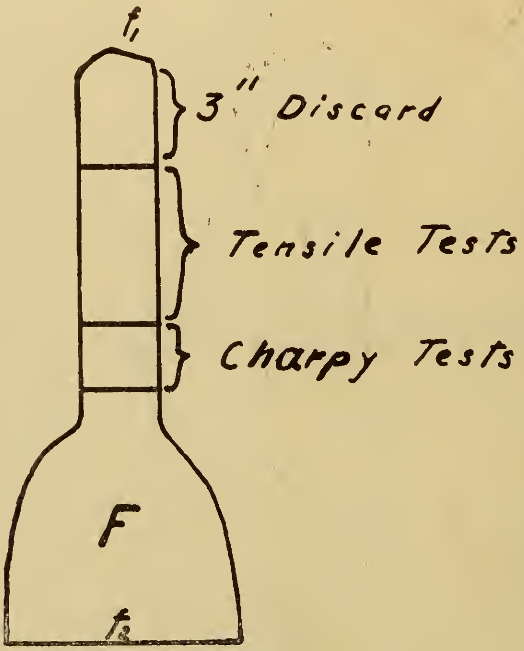

Fig. 9.—Position of Tests from Ingots after Forging.

TABLE V.—*Experiment* 2. *Specific Gravity Tests from S, Fig* 8.

| Ingot No. | Specific Gravity. | Average Specific Gravity. | Deoxidiser Used. | Order of Deoxidisers as regards Specific Gravity. |
|---|---|---|---|---|
| 1<br>2<br>3 | 7·765<br>7·773<br>7·768 | 7·769 | Fe.C.Ti. | 2 or 3 |
| 5<br>6 | 7·773<br>7·732 | 7·753 | Fe.Mn. | 4 |
| 7<br>8<br>9 | 7·775<br>7·775<br>7·770 | 7·773 | Fe.Ti.<br>carbon-free | 1 |
| 11<br>12 | 7·746<br>7·745 | 7·746 | Fe.Si. | 5 |
| 13<br>14<br>15 | 7·764<br>7·776<br>7·766 | 7·769 | Al | 3 or 2 |

*Forging.*—One quarter of each ingot (see sketch, Fig. 9) was forged down to 2 inches round under a steam-hammer after heating to the usual forging temperature.

*Annealing.*—Pieces were cut from the upper half of each half ingot A (see sketch, Fig. 8), the pieces being about 2 inches square and about 7 inches long. These were heated in a semi-muffle type oil-fired shop furnace to 850° C., held for one hour, and cooled in air. All thirteen pieces were removed from the furnace within two minutes, so that the rate of cooling of all of them was practically the same. These pieces, together with pieces of about the same size from the forged metal, were then heated to 850° C., held thirty minutes, and cooled in air. They were then reheated to 650° C. for about thirty minutes and cooled in air.

The bars from the forged metal were chosen as follows : Three inches were discarded from the end of the bar representing the upper end of the lower half-ingot (see sketch, Fig. 9). A piece long enough for one tensile and four Charpy test-pieces was then cut off and annealed as described above.

*Physical Tests.*—Tensile test-pieces and Charpy impact test-pieces were cut from the annealed material and subjected to tensile and Charpy impact tests respectively, with the results given in Tables VI. to XI. inclusive.

Table VI.—*Experiment* 2. *Tensile Tests of Annealed Cast Specimens.*

| Ingot No. | Elastic Limit. Lbs. per Sq. In. | Tensile Strength. Lbs. per Sq. In. | Elongation per Cent. in 2 Inches. | Contraction of Area per Cent. | Appearance of Fracture. |
|---|---|---|---|---|---|
| 1 | 46,000 | 74,000 | 11·0 | 24·0 | Amorphous, with patches of granular spots. |
| 2 | 44,500 | 69,500 | 9·0 | 13·3 | Amorphous, with patches of granular spots. |
| 3 | 47,500 | 67,500 | 8·5 | 16·9 | Amorphous, with dark-coloured spot at circumference. |
| 5 | 46,000 | 75,000 | 11·0 | 20·5 | Amorphous, with dark-coloured spot at circumference. |
| 6 | 45,500 | 65,500 | 7·5 | 20·5 | Amorphous, with patches of dark-coloured metal near circumference. |
| 7 | 49,000 | 65,500 | 5·5 | 9·5 | Amorphous, with granular spot at circumference. |
| 8 | 49,500 | 68,000 | 5·5 | ... | Amorphous. Fractured outside gauge marks. |
| 9 | 38,000 | 49,000 | 6·0 | 13·3 | Amorphous, with dark-coloured patch at circumference. |
| 11 | 46,000 | 70,500 | 9·5 | 13·3 | Amorphous, with granular and light-coloured spots. |
| 12 | 49,000 | 70,500 | 9·0 | 16·9 | Amorphous, with granular spots near circumference. |
| 13 | 41,500 | 55,000 | 5·0 | 5·7 | Amorphous, with granular spots near circumference. |
| 14 | 37,500 | 48,500 | 4·5 | 9·5 | Amorphous, with dark-coloured patches at circumference. |
| 15 | 39,000 | 65,500 | 9·5 | 13·3 | Amorphous. |

Diameter of above specimens = 0·505 inch = 0·20 square inch.

Table VII.—*Average Physical Tests* (*Annealed Cast Metal*). *Calculated from Table VI.*

| Ingot No. | Deoxidiser Used. | Average Elastic Limit. | Average Tensile Strength. Lbs. per Sq. In. | Average Elongation per Cent. in 2 Inches. | Average Contraction of Area per Cent. | Order of Deoxidisers as regards Physical Properties. | |
|---|---|---|---|---|---|---|---|
| | | | | | | Tensile Strength. | Elongation. |
| 1, 2, 3 | Fe.C.Ti. | 46,000 | 70,300 | 9·5 | 18·1 | 2 | 1 |
| 5, 6 | Fe.Mn. | 45,800 | 70,000 | 9·2 | 20·5 | 3 | 3 |
| 7, 8, 9 | Fe.Ti.carbon-free | 45,500 | 60,800 | 5·7 | 11·4 | 4 | 5 |
| 11, 12 | Fe.Si. | 47,500 | 70,500 | 9·3 | 15·1 | 1 | 2 |
| 13, 14, 15 | Al. | 39,300 | 56,300 | 6·3 | 9·3 | 5 | 4 |

### TABLE VIII.—*Experiment 2. Tensile Tests of Annealed Forged Steel Specimens.*

| Ingot No. | Elastic Limit. Lbs. per Sq. In. | Tensile Strength. Lbs. per Sq. In. | Elongation per Cent. in 2 Inches. | Contraction of Area per Cent. | Appearance of Fracture. |
|---|---|---|---|---|---|
| 1 F | 47,500 | 82,500 | 27·5 | 49·1 | Silky. |
| 2 F | 52,000 | 82,000 | 29·0 | 51·9 | ,, |
| 3 F | 51,000 | 81,500 | 28·5 | 51·9 | ,, opened seams in stem. |
| 5 F | 48,000 | 83,500 | 25·5 | 46·2 | ,, ,, ,, ,, |
| 6 F | 49,000 | 79,000 | 30·5 | 54·6 | ,, ,, ,, ,, |
| 7 F | 46,000 | 77,000 | 31·0 | 57·2 | ,, ,, seam ,, |
| 8 F | 48,500 | 78,000 | 31·5 | 57·2 | ,, ,, seams ,, |
| 9 F | 50,500 | 84,000 | 26·5 | 46·2 | ,, open seam at centre. |
| 11 F | 52,500 | 82,500 | 29·0 | 54·6 | ,, |
| 12 F | 53,500 | 84,500 | 28·5 | 51·9 | ,, open seam in stem. |
| 13 F | 47,000 | 78,500 | 29·5 | 57·2 | ,, ,, ,, ,, |
| 14 F | 48,500 | 78,000 | 31·0 | 54·6 | ,, ,, ,, ,, |
| 15 F | 44,500 | 79,500 | 29·5 | 51·9 | ,, ,, ,, ,, |

Diameter of above specimens = 0·505 inch = 0·20 square inch.

### TABLE IX.—*Average Physical Tests (Annealed Forged Metal). Calculated from Table VIII.*

| Ingot No. | Deoxidiser Used. | Average Elastic Limit. | Average Tensile Strength. Lbs. per Sq. In. | Average Elongation per Cent. in 2 Inches. | Average Contraction of Area per Cent. | Order of Deoxidisers as regards Physical Properties. | |
|---|---|---|---|---|---|---|---|
| | | | | | | Tensile Strength. | Elongation. |
| 1 F<br>2 F<br>3 F | Fe.C.Ti. | 50,200 | 82,200 | 28·3 | 51·0 | 2 | 4 |
| 5 F<br>6 F | Fe.Mn. | 48,500 | 81,300 | 28 | 50·4 | 3 | 5 |
| 7 F<br>8 F<br>9 F | Fe.Ti. carbon-free | 48,300 | 79,700 | 29·7 | 53·5 | 4 | 2 |
| 11 F<br>12 F | Fe.Si. | 53,000 | 83,500 | 28·8 | 53·3 | 1 | 3 |
| 13 F<br>14 F<br>15 F | Al. | 46,700 | 78,700 | 30·0 | 54·6 | 5 | 4 |

TABLE X.—*Charpy Tests on Annealed Cast Steel.*

| Deoxidiser. | Ingot No. | Annealed Cast Steel. | | | | Relative Order of Deoxidisers. |
|---|---|---|---|---|---|---|
| | | Foot-pounds per Square Inch. | | | | |
| | | Max. | Min. | Average. | General Average. | |
| Fe.C.Ti. | 1 | 147·5 | 104·0 | 119·3 | 119·0 | 2 |
| | 2 | 124·0 | 120·0 | 121·0 | | |
| | 3 | 134·5 | 105·5 | 116·7 | | |
| Fe.Mn. | 4 | ... | ... | ... | 116·8 | 3 |
| | 5 | 120·0 | 97·7 | 109·0 | | |
| | 6 | 140·4 | 105·5 | 124·6 | | |
| Carbon-free Fe.Ti. | 7 | 113·6 | 92·0 | 100·6 | 94·6 | 5 |
| | 8 | 120·2 | 77·8 | 91·8 | | |
| | 9 | 120·5 | 70·2 | 91·5 | | |
| Fe.Si. | 10 | ... | ... | ... | 131·5 | 1 |
| | 11 | 127·0 | 98·5 | 108·9 | | |
| | 12 | 167·5 | 135·2 | 154·2 | | |
| Aluminium | 13 | 121·0 | 79·0 | 103·3 | 114·9 | 2 |
| | 14 | 149·6 | 105·6 | 125·2 | | |
| | 15 | 133·0 | 91·9 | 116·3 | | |

Four pieces from each ingot were tested.

TABLE XI.—*Charpy Tests on Annealed Forged Steel.*

| Deoxidiser | Ingot No | Annealed Forged Steel. | | | | Relative Order of Deoxidisers. |
|---|---|---|---|---|---|---|
| | | Foot-pounds per Square Inch. | | | | |
| | | Max. | Min. | Average. | General Average. | |
| Fe.C.Ti. | 1 | 196·6 | 164·0 | 184·3 | 188·0 | 5 |
| | 2 | 188·2 | 157·0 | 178·2 | | |
| | 3 | 246·8 | 165·6 | 201·4 | | |
| Fe.Mn. | 4 | ... | ... | ... | 221·5 | 3 |
| | 5 | 229·0 | 212·0 | 221·0 | | |
| | 6 | 231·2 | 204·0 | 222·0 | | |
| Carbon-free Fe.Ti. | 7 | 315·2 | 237·2 | 266·3 | 287·3 | 2 |
| | 8 | 318·0 | 246·0 | 279·6 | | |
| | 9 | 376·0 | 288·0 | 316·0 | | |
| Fe.Si. | 10 | ... | ... | ... | 208·0 | 4 |
| | 11 | 220·8 | 189·8 | 200·3 | | |
| | 12 | 248·0 | 188·2 | 215·8 | | |
| Aluminium | 13 | 384·0 | 332·8 | 359·1 | 340·1 | 1 |
| | 14 | 368·0 | 302·0 | 336·7 | | |
| | 15 | 354·2 | 279·4 | 324·2 | | |

Four pieces from each ingot were tested.

It will be noted that in the tensile and Charpy tests the differences between the averages of the various groups of ingots are often less than the differences between many of the physical properties in the same group, the term "group" being understood to include the two or three ingots cast with the same deoxidiser.

*Segregation.*—Carbon determinations were made in duplicate by the direct combustion process from five of the ingots (Nos. 1, 6, 9, 12, 15), and the results are shown in Plates XVIII. to XXII.

In Ingot No. 1, made with ferro-carbon-titanium, the tests have not brought out any segregation of carbon; in fact there may be said to be a slight negative segregation since the average carbon at the bottom of the pipe (drill-hole No. 6, Plate XVIII.) is 0·366 per cent., while the average at drill-hole No. 4 at the outside of the ingot is 0·399 per cent., and that at drill-hole No. 15 is 0·385 per cent.; and the average carbon from the five drill-holes on the axis of the ingot is 0·368 per cent., while the average carbon at the five drill-holes on the outside of the ingot is 0·391 per cent. The same thing is true of Ingot No. 6, made with ferro-manganese addition, in which the carbon at the bottom of the pipe is 0·372 per cent. (drill-hole No. 6, Plate XIX.), while at the corresponding point on the outside of the ingot (drill-hole No. 4) the carbon is 0·403 per cent. The average carbon from the five holes representing the axis of the ingot is 0·382 per cent., while the average carbon at the outside of the ingot is 0·397 per cent. The same remarks apply also in general to Ingot No. 9, made with carbon-free ferro-titanium. The carbon at the bottom of the pipe is 0·366 per cent. (drill-hole No. 6, Plate XX.), while the carbon at the corresponding point on the outside (drill-hole No. 4) is 0·394 per cent., and the average carbon in the axis is 0·371 per cent., while the average carbon on the outside is 0·377 per cent. The difference between the inside and the outside in this ingot, however, is not so well marked as in the others. But at drill-hole No. 3, situated near the pipe, positive segregation is shown, the carbon being 0·442 per cent. In Ingot No. 12, made with ferro-silicon, there is a slight segregation of carbon at the bottom of the pipe, the average carbon at drill-hole No. 6, Plate XXI., being 0·609 per cent., while the carbon at the corresponding point on the outside (drill-hole No. 4) is 0·375 per cent. In this ingot the average axial carbon is 0·407 per cent., while the average carbon at the outside is 0·361 per cent. In Ingot No. 15, made with aluminium, there is also a distinct positive segregation, the carbon at the lower end of the pipe (drill-hole No. 6, Plate XXII.) being 0·528 per cent., while the carbon at the corresponding point on the outside of the ingot (drill-hole No. 4) is 0·396 per cent. The average axial carbon in this ingot is 0·408 per cent., while the carbon at the outside of the ingot averages 0·382 per cent.

If we consider each ingot to be made up of three concentric cylinders, the inner one solid with a diameter of 2 inches, the second one hollow with inside diameter of 2 inches and outside diameter of 4 inches, and the third hollow with inside diameter of 4 inches and outside diameter of 7 inches, it is easy to calculate the approximate carbon content of each ingot by assigning to the central cylinder of metal a carbon content equal to the mean of the axial carbon determinations, to the second cylinder a carbon content equal to the mean of the analyses between the axis and the outside, and to the outside cylinder the mean of the analyses taken at the outside.

The following table gives the result of such a calculation and shows the influence of the various deoxidisers on segregation and their relative merits based on this criterion:

TABLE XII.—*Relative Value of Deoxidisers as regards Prevention of Segregation.*

| Kind of Deoxidiser. | Order of Deoxidiser. | Percentage Segregation. |
|---|---|---|
| Fe.Mn. | 1 | + 2 |
| Fe.C.Ti. | 2 | − 5 |
| Fe.Ti. (carbon-free) | 3 | + 18 |
| Al. | 4 | + 44 |
| Fe.Si. | 5 | + 64 |

*Extraction of Gases.*—It was hoped that the extraction of gases, at a high temperature *in vacuo*, from samples of the various ingots would throw some light on the action of the so-called deoxidisers, especially since Thomas Baker in his paper entitled "Gases Occluded in Steel"[1] showed that in comparing cast crucible steel of about 0·80 per cent. to 0·90 per cent. carbon, with and without the addition of "a small amount of aluminium," the former gave off twice the volume of total gases obtained from the latter during 110 hours' heating at 1000° C. His heatings were made for ten days at about eleven hours a day. A brief summary of Baker's results is given below in Table XIII.

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[1] *Iron and Steel Institute: Carnegie Scholarship Memoirs*, 1909, vol. i. p. 219.

TABLE XIII.—*Summary of Baker's Results.*

| Kind of Steel. | CC. Total Gases per Gramme of Steel. | $CO_2$ per Cent. | $H_2$ per Cent. | CO per Cent. | $CH_4$ per Cent. | $N_2$ per Cent. |
|---|---|---|---|---|---|---|
| 1. Sound steel, 0·90 per cent. carbon . . . . | 1·33 | 1·68 | 52·03 | 45·53 | 0·72 | 0·04 |
| 2. Unsound steel, 0·81 per cent. carbon . . . . | 0·665 | 0·89 | 54·62 | 42·41 | 1·73 | 0·37 |

Weight of steel sample—No. 1, 69·31 grammes.
„ „ „ No. 2, 63·261 „

If proper apparatus could have been had for collecting the gases given off from the molten steel, a better basis of comparison between deoxidisers would doubtless have been established, but this was impracticable. This point, however, has been called to the attention of the U.S. Bureau of Standards, who may carry out some experiments along this line with molten steel. It was decided in the present work to extract the gases at 1000° C. for thirty hours, since it was found by experiment that the rate of evolution of gas after that time was very low.

The apparatus used in this work follows closely that employed by Baker.

The heating unit consisted of an alundum tube wound with No. 18 nichrome wire, the entire winding having a resistance of 19 ohms. The alundum tube was 12 inches in length, the internal diameter being 1¼ inch with walls $\frac{3}{16}$ inch thick. A fused silica tube, glazed both inside and outside, was placed concentrically in the alundum tube, the length of the silica tube being 24 inches with an internal diameter of ⅞ inch. In the work by Baker a porcelain tube was used, but it is the author's opinion that fused silica has several advantages over porcelain for this work. The ends of the silica tube were closed with rubber stoppers, connections being made through one stopper to the pumping system. The other stopper was solid.

At the beginning of the work the thermocouple was placed inside the silica tube, access being made by means of a two-hole stopper, the wires of the couple being fused into glass tubes where they passed through the two-hole stopper. Two disadvantages were present by using this method : (1) The temperature of the interior of the silica tube lagged considerably behind the temperature of the heating unit, thus making accurate control impossible ; (2) the occluded gases of the couple and insulating tubes were a source of error.

Since constant temperature was sought rather than actual temperature, the couple was then placed between the silica tube and the heating unit, for there the least temperature change in the furnace would show at once and could be corrected by using more or less current as necessary without affecting the temperature inside the tube, since a long series of simultaneous readings of temperature in the interior of the silica tube and the space between the silica tube and walls of the furnace showed that at constant temperature the difference was negligible after ten minutes had elapsed. It seems evident, therefore, that when constant temperature is required over long periods the method used was not only permissible but had certain advantages, among which is convenience of manipulation.

All temperature measurements were made with a platinum-platinum 10 per cent. rhodium couple, the electromotive force being read by a Leeds & Northrup portable potentiometer. This arrangement permits of an accuracy of ± 5° C.

The pumping system consisted of a Géryk oil-sealed pump of the plunger type for rough work and a Toepler mercury pump for the fine work. Either pump could be brought into connection with the tube by manipulation of the stop-cocks A and B (Fig. 15).

Gases were collected in the collecting-bottle of special design shown in the drawing (Fig. 15) and from there were drawn to the burette for analysis. The photograph (Plate XXIII.) will give an idea of the apparatus assembled.

The details of an actual typical experiment will next be described, which will be followed by the report of some blank tests.

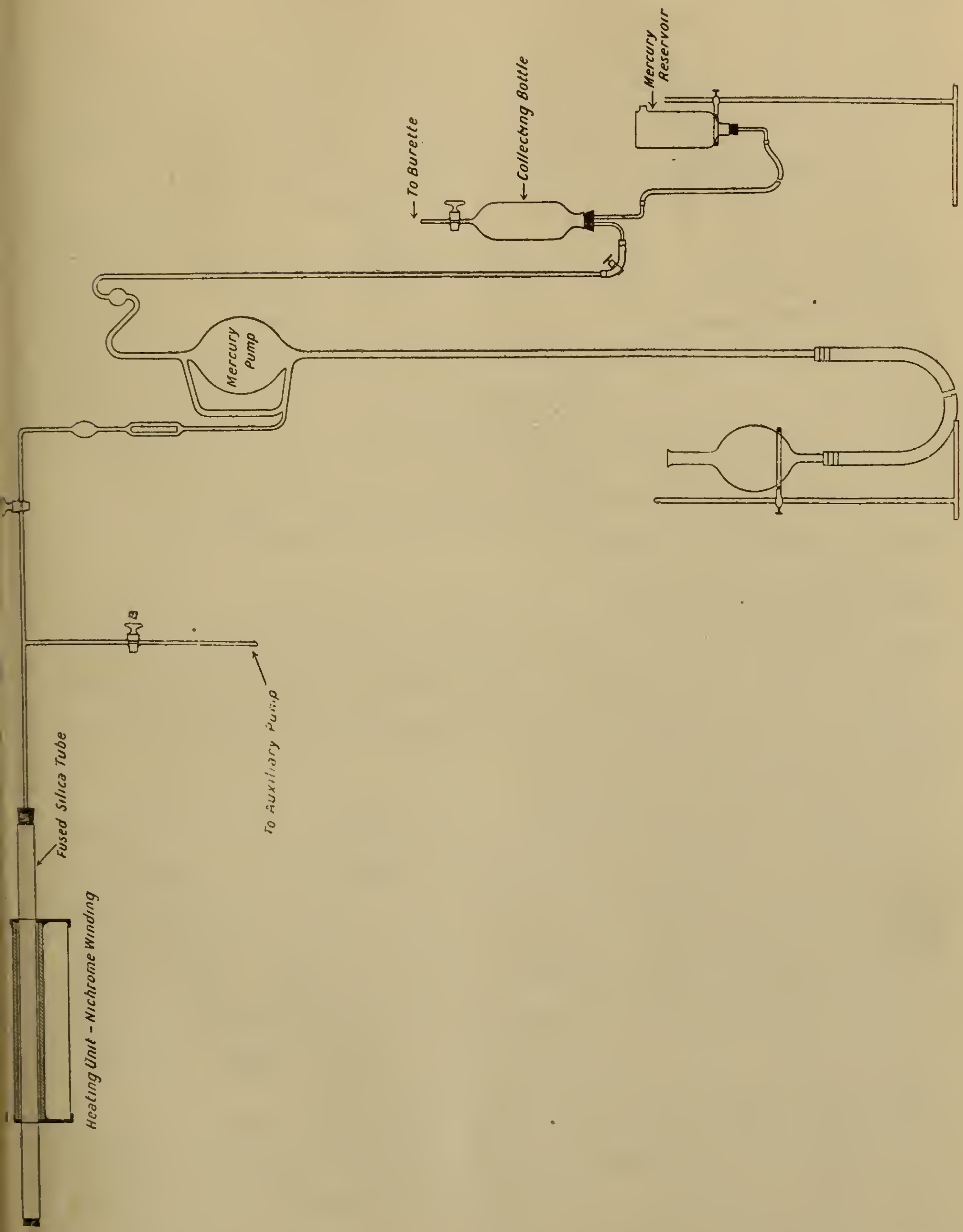
To Burette
Collecting Bottle
Mercury Reservoir
Mercury Pump
Fused Silica Tube
To Auxiliary Pump
Heating Unit - Nichrome Winding

Fig. 15.

The specimens used varied in weight from 40 to 50 grammes, most of them weighing from 47 to 50 grammes.

The sample numbers correspond with the ingot numbers in Experiment 2.

A specimen was thoroughly cleaned and washed in benzine and alcohol. After its weight had been determined, it was placed in the silica tube. The stopper was inserted and all joints were given a coating of shellac, to insure tightness. The ends of the silica tube were water-cooled to prevent the corks from overheating.

The cock at A was closed and cock B opened. The roughing pump was then operated for thirty minutes. This pump gave on all experiments a vacuum better than 0·1 millimetre. At the end of thirty minutes B was closed and A opened. Pumping was continued for thirty minutes with the mercury pump. The pinch-cock between the collecting-bottle and the pump was then closed, the gas in the collecting-bottle being driven out by raising the mercury reservoir connected with the latter. The pinch-cock was then opened and the heating current turned on. The heating current was controlled by a carbon block rheostat and an ammeter in the circuit.

The time of heating from atmospheric temperature to 1000° C. was one hour, and this figure was always kept constant.

When the temperature reached 1000° C., the current was reduced to 5·65 amperes, which maintained the temperature of 1000° C. within 5° C.

The temperature was held there for ten hours. This constituted one period. At the end of ten hours, the furnace was allowed to cool to atmospheric temperature. Whenever the pressure in the tube rose to 3 millimetres, the mercury pump was operated and the gas collected. On heating, gases were given off slowly for about forty minutes and after that very rapidly. The period of rapid evolution of gases corresponds evidently with the thermal critical range. The temperature at which the rapid evolution began was apparently between 750° and 850° C.

At the end of a period the gases were passed into a burette and analysed. The ordinary methods of gas analysis were used.

The above operation was repeated twice, making three periods in all. The gases collected then were the gases given off by three ten-hour periods at 1000° C. and the gases given off in heating to and cooling from that temperature for three successive times.

It was evident from the work of Baker and others that considerable gas would cling to the sides of the tube even at high vacuums. Several blanks therefore were run with the furnace cold and hot respectively. The blanks with the cold furnace served to show that the connections were tight. The pressure would rise slightly for forty-eight hours or more, but from that time on was stationary within the limits of observation.

The blanks on a three-period run were very interesting. The average of three such blanks gave the following result :

| | Cubic Centimetres. |
|---|---|
| Period 1 | 4·1 |
| ,, 2 | 1·2 |
| ,, 3 | 1·1 |

*Average Analysis.*

| | Per Cent. |
|---|---|
| $CO_2$ | 3·5 |
| $O_2$ | 8·5 |
| $H_2$ | 3·0 |
| $N_2$ | 8·5 |

After the apparatus had been used for several determinations other blanks were run, and as was to be expected the hydrogen content rose to some extent, since it is difficult to remove the last traces of adsorbed hydrogen. Traces of $CH_4$ were also present.

The data obtained from the several samples has been reduced to standard conditions of 760 millimetres pressure and 0° C. Tables for each sample are given (Tables XIV. to XXIV.). In the upper half of each table the number of cubic centimetres of each gas for each period can be found by passing along the table horizontally after the number of the period. A row is also provided for the sum of the three periods. The last vertical column shows the total volume for each period and also the total volume of gas collected.

The lower half of each table is constructed in the same manner and shows percentage by volume, the last column marked " Per Cent. Total of Sum " showing what per cent. of the total gas collected was given off in any period.

A special table (Table XXV.) is also provided showing the summation of the results. A column has been introduced showing volume of gas per gramme of metal. It has been assumed by Baker, and in this report, that gas evolved is a function of mass.

No doubt this is true to some extent, but the gas evolved may also be a function of the surface exposed.

TABLE XIV. *Sample* *1. (Fe.C.Ti.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 22·23 | 0·00 | 23·25 | 1·12 | 46·60 |
| 2 | 0·19 | 10·23 | 0·19 | 10·32 | 0·74 | 21·67 |
| 3 | 0·00 | 7·25 | 0·19 | 6·98 | 0·65 | 15·07 |
| Sum | 0·19 | 39·71 | 0·38 | 40·55 | 2·51 | 83·34 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 47·70 | 0·00 | 49·89 | 2·41 | 55·41 |
| 2 | 0·88 | 47·74 | 0·88 | 47·56 | 3·54 | 26·00 |
| 3 | 0·00 | 48·83 | 1·27 | 46·53 | 3·87 | 18·09 |
| Sum | 0·23 | 47·65 | 0·46 | 48·66 | 3·00 | 100·00 |

Weight of sample, 48·39 grammes.

TABLE XV.—*Sample* * 3. (Fe.C.Ti.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·18 | 13·89 | 0·09 | 14·35 | 0·92 | 29·43 |
| 2 | 0·27 | 3·04 | 0·09 | 3·40 | 0·64 | 7·44 |
| 3 | 0·09 | 2·02 | 0·00 | 2·39 | 0·83 | 5·33 |
| Sum | 0·54 | 18·95 | 0·18 | 20·14 | 2·39 | 42·20 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·61 | 47·13 | 0·13 | 48·76 | 3·19 | 69·74 |
| 2 | 3·63 | 40·86 | 1·21 | 45·70 | 8·60 | 17·63 |
| 3 | 1·69 | 37·90 | 0·00 | 44·84 | 15·57 | 12·631 |
| Sum | 1·28 | 44·90 | 0·43 | 47·72 | 5·67 | 100·00 |

Weight of sample, 51·9679 grammes.

## Table XVI.—*Sample* *5. (Fe.Mn.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 22·32 | 0·37 | 22·41 | 1·21 | 46·31 |
| 2 | 0·00 | 7·91 | 0·09 | 7·91 | 0·65 | 16·56 |
| 3 | 0·00 | 5·98 | 0·14 | 6·16 | 0·64 | 12·92 |
| Sum | 0·00 | 36·21 | 0·60 | 36·48 | 2·50 | 75·79 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 48·20 | 0·80 | 48·39 | 2·51 | 61·95 |
| 2 | 0·00 | 47·76 | 0·54 | 47·76 | 3·94 | 21·85 |
| 3 | 0·00 | 46·29 | 1·09 | 47·69 | 4·93 | 16·20 |
| Sum | 0·00 | 47·77 | 0·79 | 48·13 | 3·31 | 100·00 |

Weight of sample, 50·5972 grammes.

## Table XVII.—*Sample* *8. (Fe.Ti. carbonless.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·09 | 17·93 | 0·00 | 19·57 | 0·64 | 38·23 |
| 2 | 0·00 | 5·92 | 0·00 | 6·64 | 0·55 | 13·11 |
| 3 | 0·19 | 3·16 | 0·09 | 3·72 | 0·65 | 7·81 |
| Sum | 0·28 | 27·01 | 0·09 | 29·93 | 1·84 | 59·15 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·23 | 46·90 | 0·00 | 51·19 | 1·91 | 64·63 |
| 2 | 0·00 | 45·15 | 0·00 | 50·65 | 4·20 | 22·16 |
| 3 | 2·43 | 40·46 | 1·15 | 47.63 | 8·33 | 13·21 |
| Sum | 0·47 | 45·66 | 0·15 | 50·60 | 3·12 | 100·00 |

Weight of sample, 47·6817 grammes.

### TABLE XVIII.—*Specimen* *9. (Fe.Ti. carbonless.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 18·58 | 0·14 | 19·50 | 0·97 | 39·19 |
| 2 | 0·00 | 4·05 | 0·09 | 4·42 | 0·74 | 9·30 |
| 3 | 0·09 | 3·28 | 0·09 | 3·91 | 0·82 | 8·10 |
| Sum | 0·09 | 25·91 | 0·32 | 27·83 | 2·53 | 56·59 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 47·41 | 0·36 | 49·75 | 2·48 | 69·24 |
| 2 | 0·00 | 43·55 | 0·96 | 47·53 | 7·96 | 16·43 |
| 3 | 1·11 | 40·49 | 1·11 | 48·27 | 9·02 | 14·33 |
| Sum | 0·16 | 45·78 | 0·57 | 49·17 | 4·32 | 100·00 |

Weight of sample, 6·4439 grammes.

### TABLE XIX.—*Sample* *12. (Fe.Si.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 15·64 | 0·24 | 17·02 | 1·14 | 34·04 |
| 2 | 0·00 | 3·68 | 0·28 | 3·86 | 1·10 | 8·92 |
| 3 | 0·00 | 3·59 | 0·00 | 4·32 | 0·64 | 8·55 |
| Sum | 0·00 | 22·91 | 0·52 | 25·20 | 2·88 | 51·51 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 46·00 | 0·71 | 50·06 | 3·23 | 66·09 |
| 2 | 0·00 | 41·35 | 3·14 | 43·37 | 12·14 | 17·32 |
| 3 | 0·00 | 41·99 | 0·00 | 50·53 | 7·48 | 16·59 |
| Sum | 0·00 | 44·49 | 1·01 | 48·93 | 5·57 | 100·00 |

Weight of sample, 47·0992 grammes.

### TABLE XX.—*Sample* *13. (Al.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·09 | 19·02 | 0·00 | 20·66 | 0·82 | 40·59 |
| 2 | 0·09 | 6·64 | 0·27 | 7·28 | 0·73 | 15·01 |
| 3 | 0·09 | 3·37 | 0·00 | 4·91 | 0·09 | 8·46 |
| Sum | 0·27 | 29·03 | 0·27 | 32·85 | 1·64 | 64·06 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·22 | 46·85 | 0·00 | 50·89 | 2·04 | 63·42 |
| 2 | 0·60 | 44·27 | 1·80 | 48·53 | 5·60 | 23·43 |
| 3 | 1·06 | 39·65 | 0·00 | 57·76 | 1·53 | 13·15 |
| Sum | 0·42 | 45·36 | 0·42 | 51·33 | 2·47 | 100·00 |

Weight of sample, 47·9093 grammes.

### TABLE XXI.—*Sample* *15. (Al.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·09 | 15·07 | 0·11 | 16·00 | 1·02 | 32·29 |
| 2 | 0·09 | 5·30 | 0·09 | 5·77 | 0·65 | 11·90 |
| 3 | 0·00 | 5·21 | 0·00 | 6·51 | 0·65 | 12·37 |
| Sum | 0·18 | 25·58 | 0·20 | 28·28 | 2·32 | 56·56 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·21 | 46·66 | 0·34 | 49·53 | 3·26 | 57·09 |
| 2 | 0·75 | 44·54 | 0·76 | 48·49 | 5·46 | 21·04 |
| 3 | 0·00 | 42·12 | 0·00 | 52·63 | 5·25 | 21·88 |
| Sum | 0·32 | 45·23 | 0·35 | 50·00 | 4·10 | 100·00 |

Weight of sample, 47·2004 grammes.

### TABLE XXII.—*Sample* *17–1. (Raw Converter Metal.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·18 | 14·72 | 1·75 | 16·00 | 1·01 | 33·66 |
| 2 | 0·28 | 4·78 | 0·28 | 4·78 | 0·83 | 10·95 |
| 3 | 0·09 | 3·72 | 0·00 | 3·81 | 0·56 | 8·18 |
| Sum | 0·55 | 23·22 | 2·03 | 24·59 | 2·40 | 52·79 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·53 | 43·73 | 5·26 | 47·54 | 2·94 | 63·75 |
| 2 | 2·56 | 43·65 | 2·56 | 43·65 | 7·58 | 20·74 |
| 3 | 1·10 | 45·50 | 0·00 | 46·58 | 6·72 | 15·51 |
| Sum | 1·04 | 43·98 | 3·84 | 46·59 | 4·55 | 100·00 |

Weight of sample, 40·1734 grammes.

### TABLE XXIII.—*Sample* 18–1. (Steel without Deoxidiser.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total. C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·74 | 15·44 | 0·37 | 14·97 | 1·49 | 33·01 |
| 2 | 0·09 | 5·21 | 0·09 | 5·77 | 0·65 | 11·81 |
| 3 | 0·09 | 3·72 | 0·19 | 4·01 | 0·85 | 8·85 |
| Sum | 0·92 | 24·37 | 0·65 | 24·75 | 2·98 | 53·67 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 2·24 | 46·78 | 1·12 | 45·36 | 4·50 | 61·45 |
| 2 | 0·76 | 44·15 | 0·76 | 48·89 | 5·46 | 21·99 |
| 3 | 1·02 | 42·04 | 2·15 | 45·32 | 9·47 | 16·56 |
| Sum | 1·71 | 45·38 | 1·21 | 46·09 | 5·61 | 100·00 |

Weight of sample, 46·3198 grammes.

Table XXIV.—*Sample* 18–2. (Steel without Deoxidiser.)

| Period. | Vol. $CO_2$. C.c. | Vol. CO. C.c. | Vol. $CH_4$. C.c. | Vol. H. C.c. | Vol. N. C.c. | Vol. Total C.c. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 16·74 | 0·12 | 16·93 | 1·30 | 35·09 |
| 2 | 0·00 | 3·81 | 0·00 | 4·09 | 0·86 | 8·76 |
| 3 | 0·00 | 3·44 | 0·00 | 4·56 | 0·09 | 8·09 |
| Sum | 0·00 | 23·99 | 0·12 | 25·58 | 2·25 | 51·94 |

| Period. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent $CH_4$. | Per Cent. H. | Per Cent. N. | Per Cent. Total of Sum. |
|---|---|---|---|---|---|---|
| 1 | 0·00 | 47·69 | 0·34 | 48·23 | 3·74 | 67·56 |
| 2 | 0·00 | 43·49 | 0·00 | 46·69 | 9·82 | 16·86 |
| 3 | 0·00 | 42·47 | 0·00 | 56·29 | 1·24 | 15·58 |
| Sum | 0·00 | 46·11 | 0·23 | 49·25 | 4·41 | 100·00 |

Weight of sample, 40·4437 grammes.

Table XXV.—*Complete Data on* 30-*hr. Run.*

| Number of Sample. | Per Cent. $CO_2$. | Per Cent. CO. | Per Cent. $CH_4$. | Per Cent. H. | Per Cent. N. | Total Volume of Gas. | Weight of Sample Grammes | Gas per gramme Metal. C.c. |
|---|---|---|---|---|---|---|---|---|
| 1 | 0·23 | 47·65 | 0·46 | 48·66 | 3·00 | 83·34 | 48·3900 | 1·72 |
| 3 | 1·28 | 44·90 | 0·43 | 47·72 | 5·67 | 42·20 | 51·9679 | 0·81 |
| 5 | 0·00 | 47·77 | 0·79 | 48·13 | 3·31 | 75·79 | 50·5972 | 1·49 |
| 8 | 0·47 | 45·66 | 0·15 | 50·60 | 3·12 | 59·15 | 47·6817 | 1·24 |
| 9 | 0·16 | 45·78 | 0·57 | 48·17 | 4·32 | 56·59 | 46·4439 | 1·22 |
| 12 | 0·00 | 44·49 | 1·01 | 48·93 | 5·57 | 51·51 | 47·0992 | 1·09 |
| 13 | 0·42 | 45·36 | 0·42 | 51·33 | 2·47 | 64·06 | 47·9093 | 1·34 |
| 15 | 0·32 | 45·23 | 0·35 | 50·00 | 4·10 | 56·56 | 47·2004 | 1·19 |
| 17-1 | 1·04 | 43·98 | 3·84 | 46·59 | 4·55 | 52·79 | 40·1734 | 1·31 |
| 18-1 | 1·71 | 95·38 | 1·21 | 46·09 | 5·61 | 53·67 | 46·3198 | 1·16 |
| 18-2 | 0·00 | 46·11 | 0·23 | 49·25 | 4·41 | 51·94 | 40·4437 | 1·28 |

Evolution curves are also shown (Charts, Figs. 17 to 27) in which the rise of pressure per hour is plotted against total time elapsed at 1000° C. The first hour of heating is included in these curves. It seems that the rate of gas evolution must be equally as important as the total gas occluded, since upon it depends the ease with which the gas may be driven off in practice. As an illustration, compare Samples 15 and 18–1. Sample 18-1 gave 1·16 cubic centimetre per gramme of metal, and Sample 15, 1·19 cubic centimetre per gramme. On comparing the evolution curves it is very evident that Sample 15 at the end of thirty-one hours is yielding gas at a rate of 2·2 millimetres rise of pressure per hour, whereas 18-1 is yielding gas at the rate of 0·9 millimetre rise of pressure per hour. In other words, 18–1 gave up its gas very readily, and at the end of the third period was nearly exhausted; 15 did not give up its gas readily but maintained a steady output.

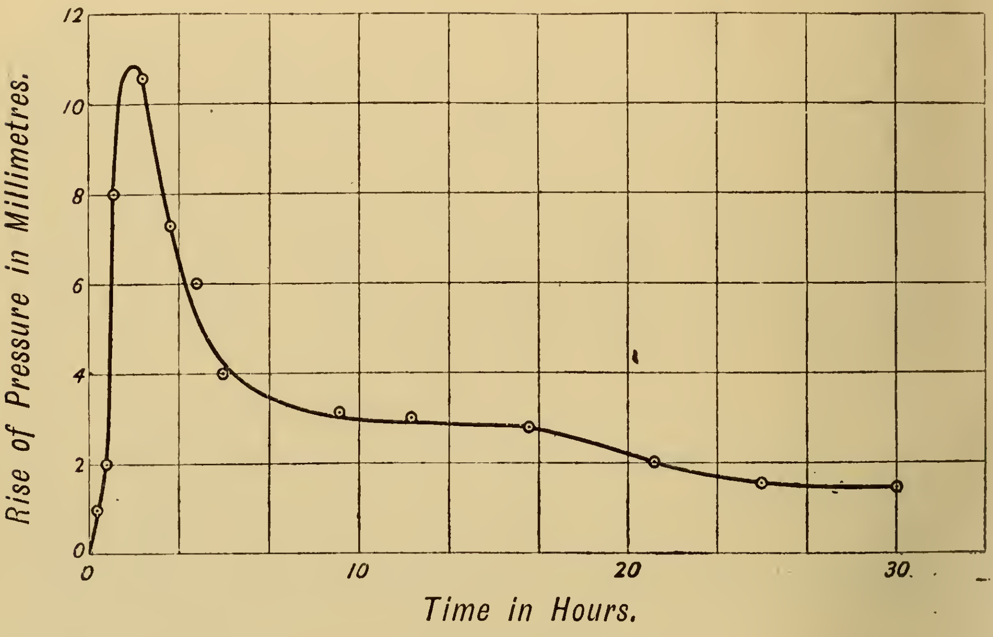

Fig. 17.—Sample 1. (Fe.C.Ti.)

Samples 1 and 3 were cast with the same deoxidiser. It is very evident that they do not check. One gives 1·72, the other 0·81 cubic centimetre per gramme.

Evolution curves for Samples 1 and 3 are as different as the gas yielded per gramme of metal. Sample 1 was yielding gas at twice the rate of Sample 3 at the end of thirty hours.

Sample 5 gave a high gas yield also. It gave off gas rapidly at first, did not fall suddenly, and at the end of the third period

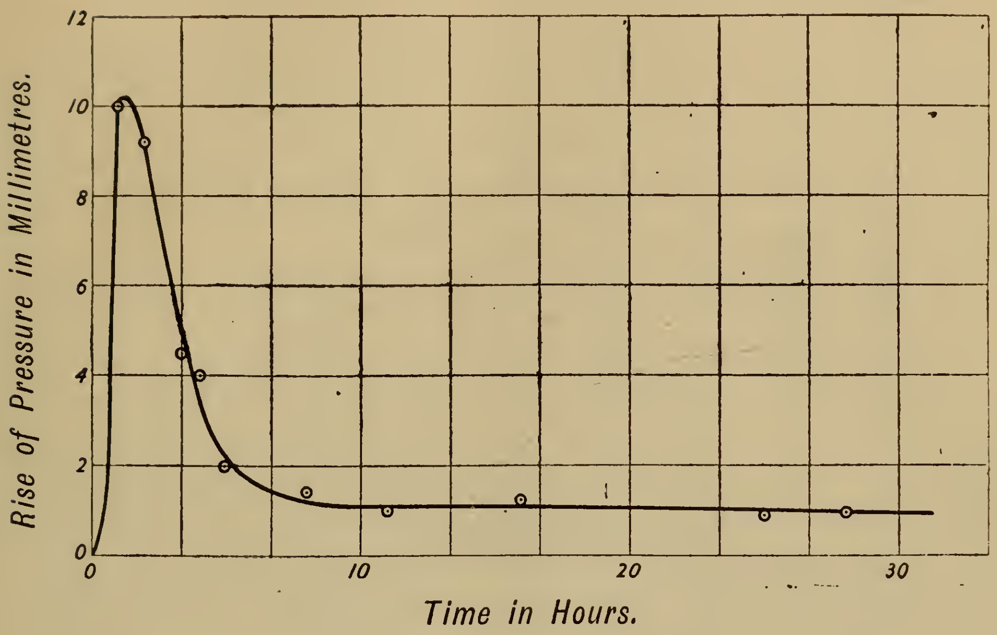

FIG. 18.—Sample 3. (Fe.C.Ti.)

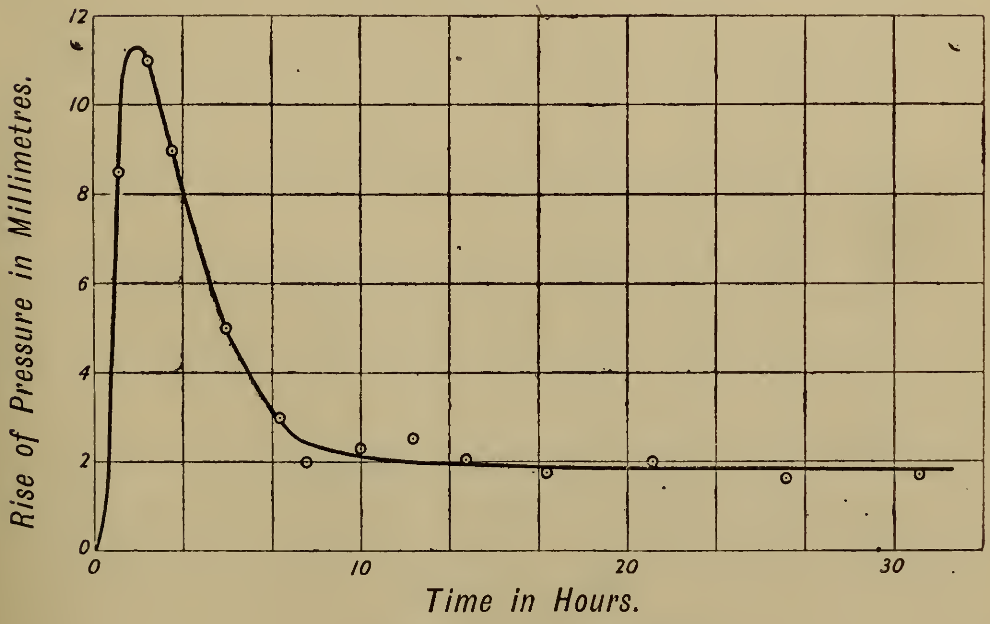

FIG. 19.—Sample 5. (Fe.Mn.)

was producing gas at the rate of 1·8 millimetre rise in pressure per hour.

Samples 8 and 9 checked well in regard to gas per gramme, Sample 8 giving 1·24 cubic centimetre and Sample 9 giving 1·22 cubic centimetre per gramme. The evolution curves do not check as well. No. 9 did not yield gas as readily as No. 8 for the first two hours, but No. 8 dropped suddenly, whereas 9 dropped more slowly, giving a very smooth, even curve.

Sample 12 yielded 1·09 cubic centimetre per gramme. Its evolution curve resembles very much that of Sample 3. At the end of the third period the rate is low and is gradually decreasing.

Samples 13 and 15 are also to be compared; No. 13 gave 1·34 cubic centimetre per gramme, No. 15, 1·19 cubic centimetre per gramme. The curve for No. 13 shows a lower rate at the end of the third period than No. 15, regardless of the fact that Sample No. 15 yielded at the end of thirty hours less gas than Sample 13. Both 13 and 15 show a high rate at the end of the third period, which would lead one to think that at the end of 100 hours, for example, they would have given a higher yield per gramme of metal as compared with 3 or 12 than appeared at the end of the thirty-hour run.

Sample 17–1, which was very full of blowholes, gave 1·31 cubic centimetre per gramme of metal. Its evolution curve has a peculiar form. The rate of evolution did not drop as suddenly as most of the other samples. Although the maximum is not as high as others, it is maintained longer. At the end of the third period the rate was still rather high.

Samples 18–1 and 18–2 gave 1·16 and 1·28 cubic centimetre per gramme. Their evolution curves are very much alike and show a low rate at the end of the third period.

An inspection of the assembled data brings out many interesting facts, a few of which can be mentioned.

Samples 8 and 9 not only check as to volume of gas per gramme, but also as to composition of gas: CO, 45·66 per cent. and 45·78 per cent.; $H_2$, 50·60 per cent. and 49·17 per cent. The hydrogen is higher in this series than in any other excepting Samples 13 and 15.

Samples 13 and 15 both run over 50 per cent. hydrogen, which is very high, their CO contents checking at 45·36 and 45·23.

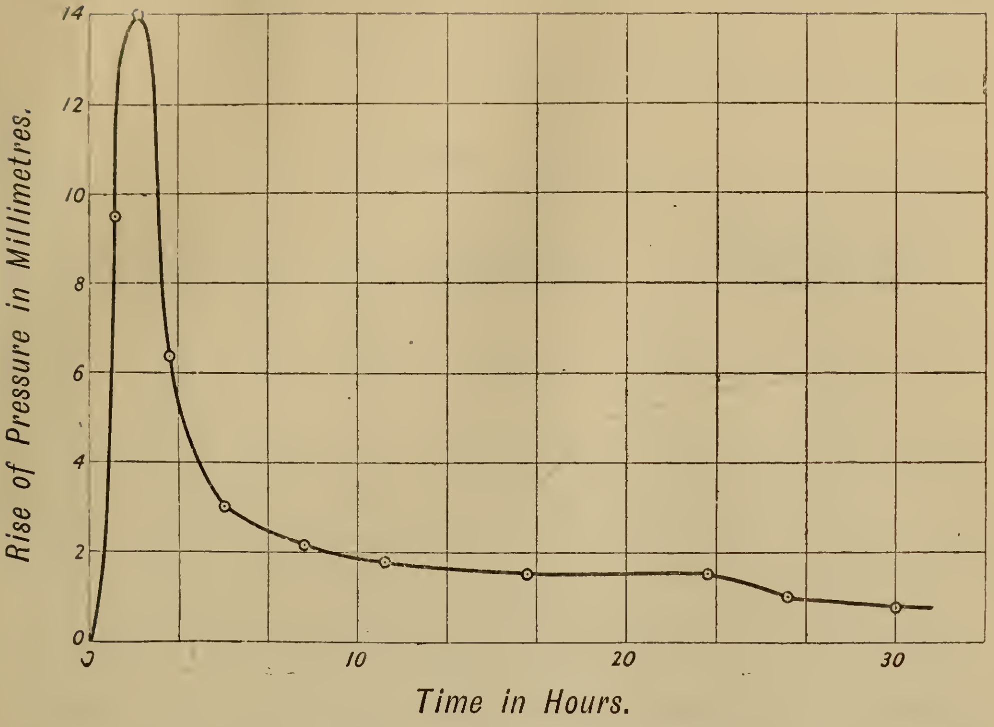

FIG. 20.—Sample 8. (Fe.Ti. carbonless.)

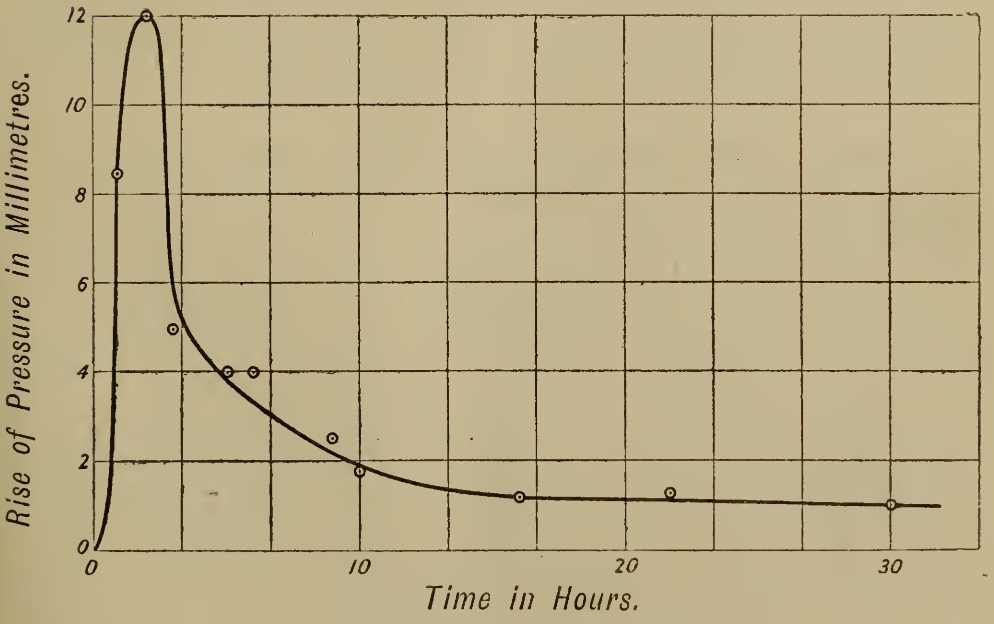

FIG. 21.—Sample 9. (Fe.Ti. carbonless.)

The following table may be of some interest. Column 1 has the samples arranged in order of volume given off per gramme; Column 2 has the samples arranged in order of per cent. $H_2$; Column 3, in order of per cent. CO.

TABLE XXVI.

| Volume per Gramme. Decreasing from Top to Bottom. | Per Cent. $H_2$. Decreasing from Top to Bottom. | Per Cent. CO. Decreasing from Top to Bottom. |
|---|---|---|
| 1 | 13 | 5 |
| 5 | 8 | 1 |
| 13 | 15 | 18-2 |
| 17-1 | 18-2 | 9 |
| 18-2 | 9 | 8 |
| 8 | 12 | 18-1 |
| 9 | 1 | 13 |
| 15 | 5 | 15 |
| 18-1 | 3 | 3 |
| 12 | 17-1 | 12 |
| 3 | 18-1 | 17-1 |

These figures appear without any apparent relation, but a little order can be brought into the chaos as follows:

Sample 1 can be rejected as its evolution curve, as well as the volume per gramme, seem irregular. Taking the means of the various groups of ingots with the same deoxidiser and arranging in order of cubic centimetre per gramme, we have

TABLE XXVII.—*Relative Order of Ingots as regards Gases Evolved.*

| Ingot No. | Cubic Centimetre per Gramme. Decreasing from Top down. | Deoxidiser Used. |
|---|---|---|
| 5 | 1·49 | Fe.Mn. |
| 17-1 | 1·31 | Raw converter metal |
| (13 and 15) | 1·27 | Al. |
| (8 and 9) | 1·23 | Fe.Ti. (carbon-free) |
| (18-1, 18-2) | 1·22 | Steel without deoxidiser |
| 12 | 1·09 | Fe.Si. |
| 3 | 0·81 | Fe.C.Ti. |

Evidently, if any valuable conclusions are to be drawn from

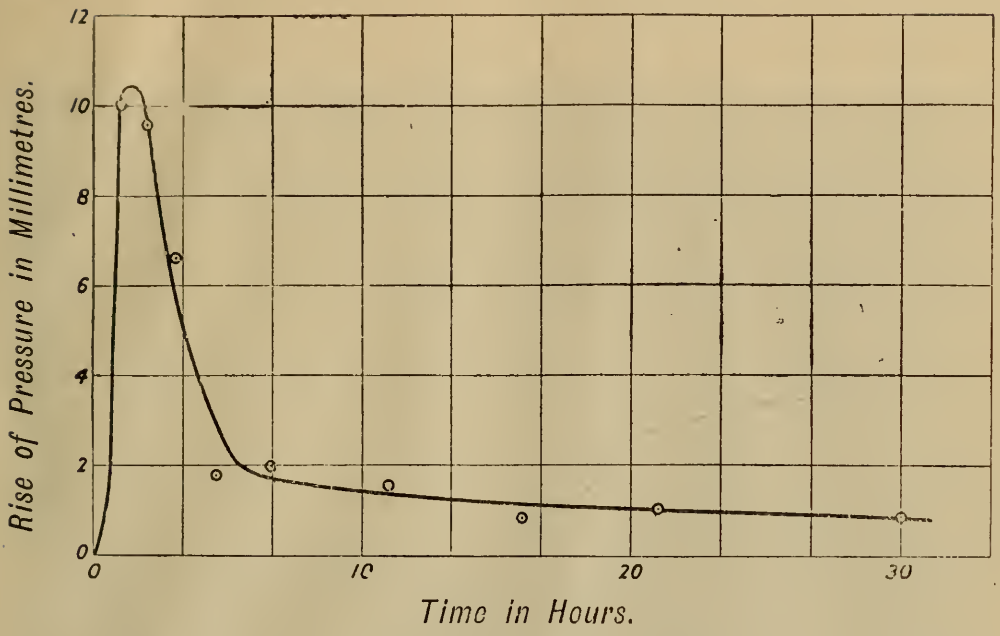

FIG. 22.—Sample 12. (Fe.Si.)

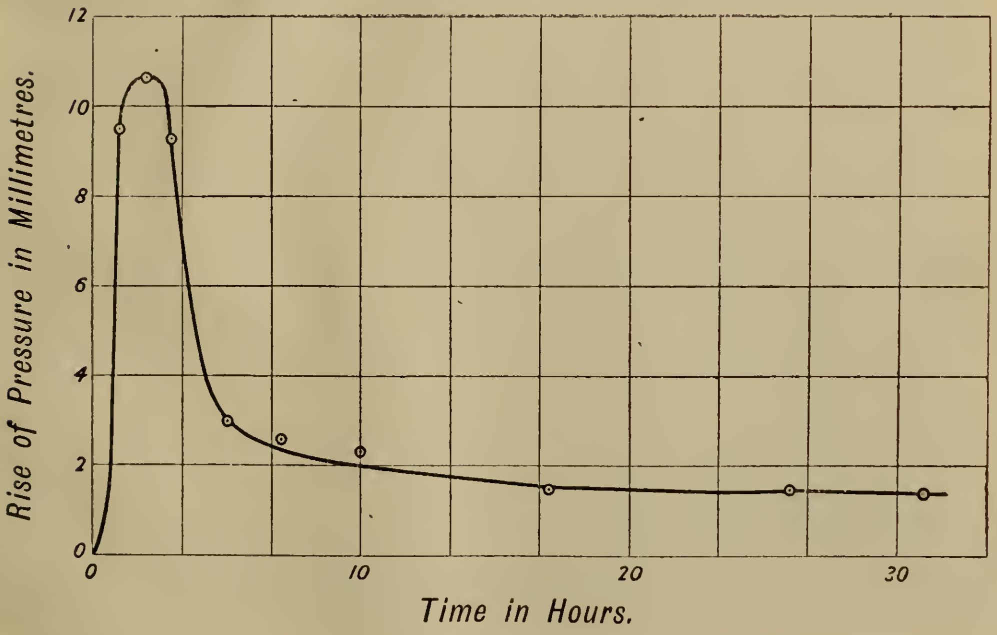

FIG. 23.—Sample 13. (Al.)

gas extraction work, there must be many more tests made from various parts of the ingot.

Comparing the average of Ingots 13 and 15, made with aluminium in these experiments, and Ingots 18–1 and 18–2, representing steel without any special deoxidiser besides the ferro-silicon and ferro-manganese needed for the analysis sought, we find that steel with aluminium gave 1·27 total gases per gramme of steel, while the steel without aluminium gave 1·22 total gases per gramme of steel, whereas it will be remembered that Baker's steel with aluminium gave 1·33 cubic centimetre total gases per gramme of steel, while his unsound steel gave 0·665 total gases per gramme of steel. It should be added that Baker tried as far as possible to open all the blowholes in his unsound steel and let out the gases contained in the holes, while no attempt was made to do this in these experiments. It should also be noted that the raw converter metal, while very unsound, gave 1·31 cubic centimetres total gases per gramme of steel, or more than any of the other ingots with the exception of Ingot 5, made with ferro-manganese as a deoxidiser.

## DISCUSSION OF RESULTS.

*The Preliminary Experiments* indicate the possibility of better results being obtained from adding the deoxidiser to the raw converter metal before recarburisation. This is a radical change from common practice, but the indications are plain that such a method might lead to valuable results.

*The Results of Experiment* 1, where no recarburiser was added, show a distinct difference in the effect of the different deoxidisers and also a difference in the various proportions of the same deoxidiser. Chart 1 and the photographs Figs. 5–23 of the author's first report show this plainly.

*Experiment* 2.—It is not entirely certain that the best proportion of each deoxidiser was used in this experiment, but some limit had to be drawn as to the number of proportions tried in Experiment 1. In two cases (Fe.C.Ti. and Fe.Ti.) the proportion used was that recommended by the manufacturers in addition to being the proportion giving the soundest ingots in Experiment 1, while the proportion of aluminium (0·14 per cent., or about

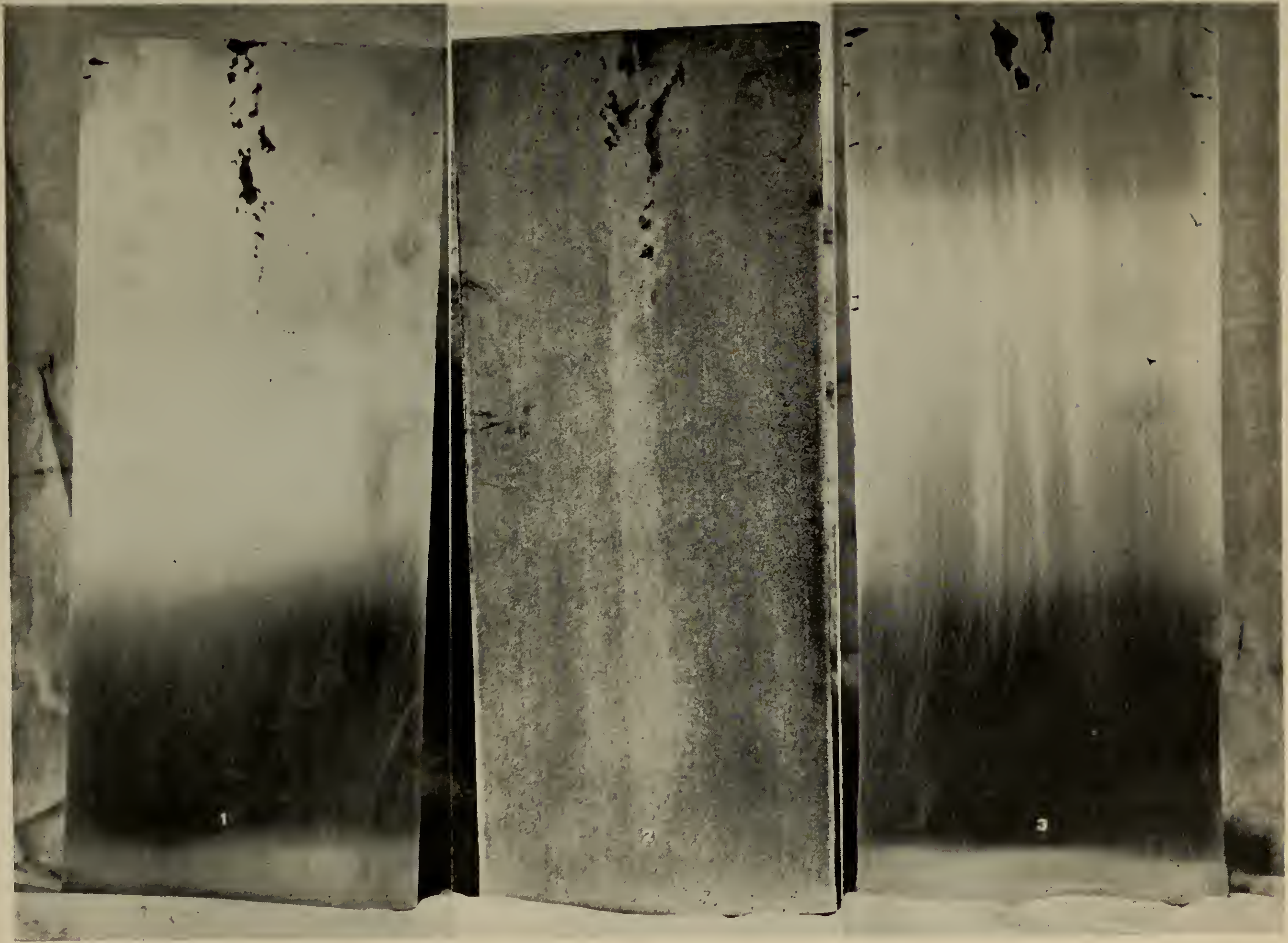

Fig. 2.—Ingots 1, 2 and 3. Exper. 2. Steel made with 0·10% Ti in form of 15% ferro-carbon titanium. Vertical sections. About one-third actual size. Ingot 2 etched with iodine.

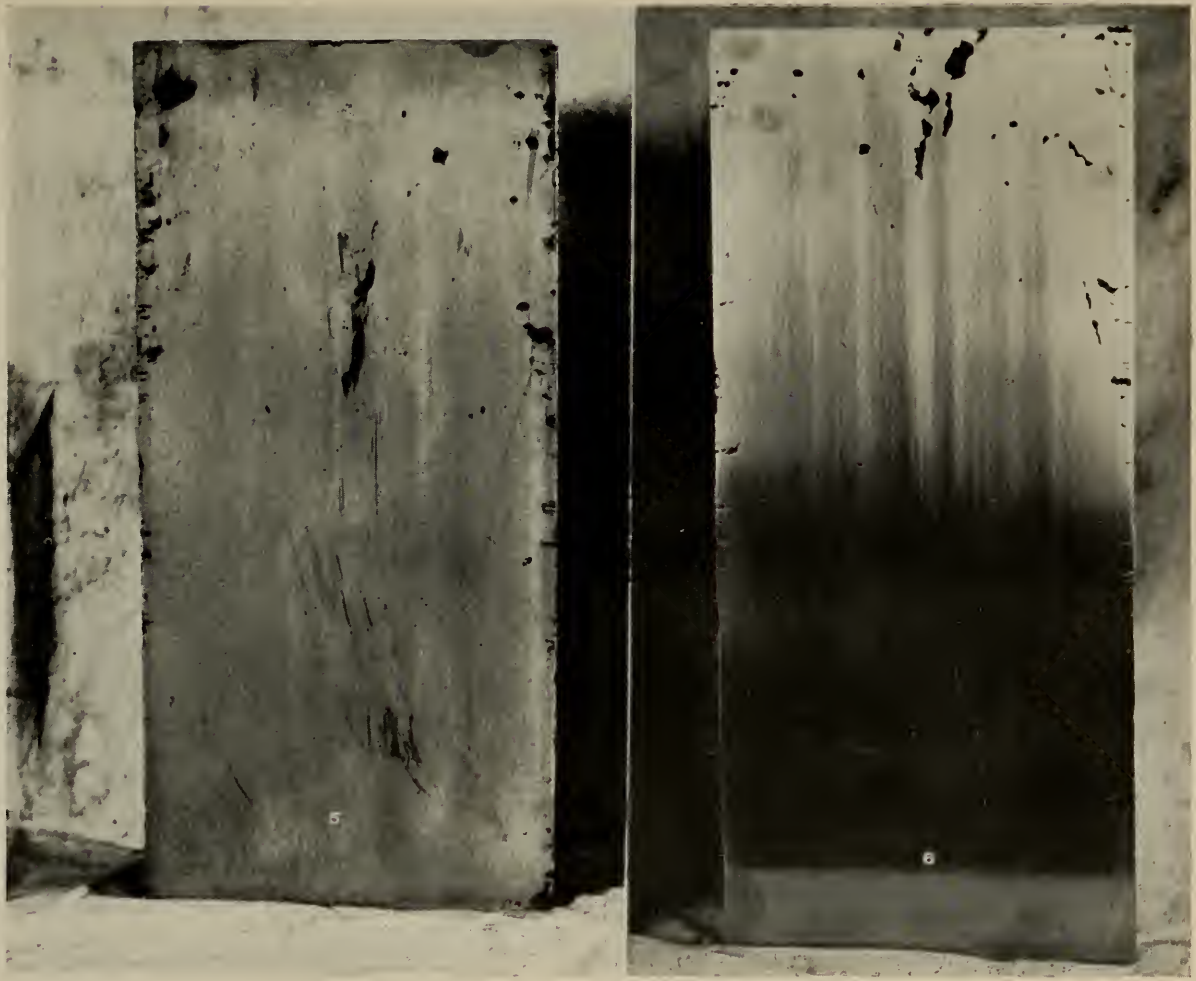

Fig. 3.—Ingots 5 and 6. Exper. 2. Steel made with about 0·50% Mn in form of 80% ferro-manganese. Vertical sections. About one-third actual size. Ingot 5 etched with iodine.

PLATE XIV

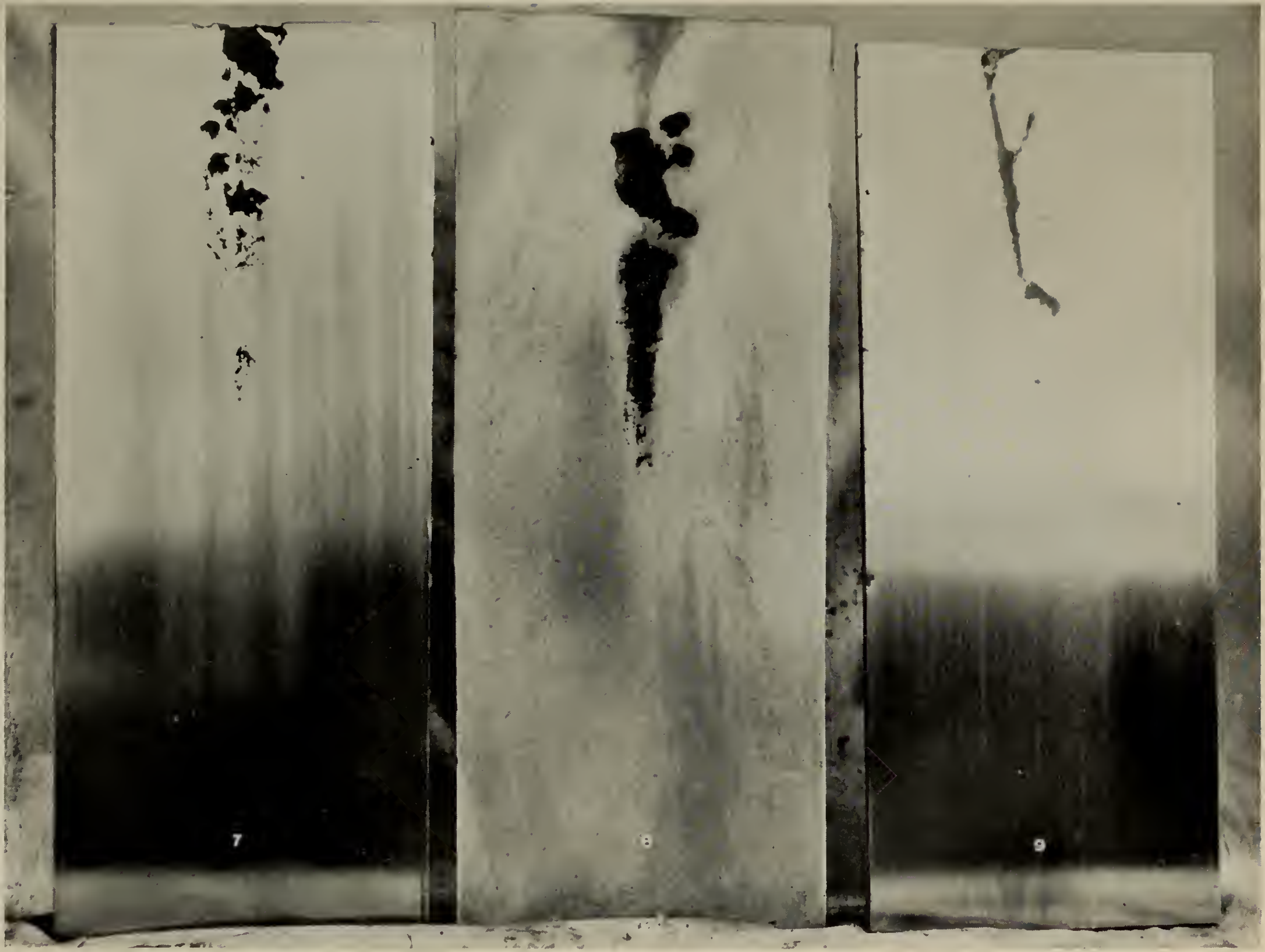

Fig. 4.—Ingots 7, 8 and 9. Exper. 2. Steel made with 0·10% Ti in form of 25% carbon-free ferro-titanium. Vertical sections. About one-third actual size. No. 8 etched with iodine.

PLATE XV

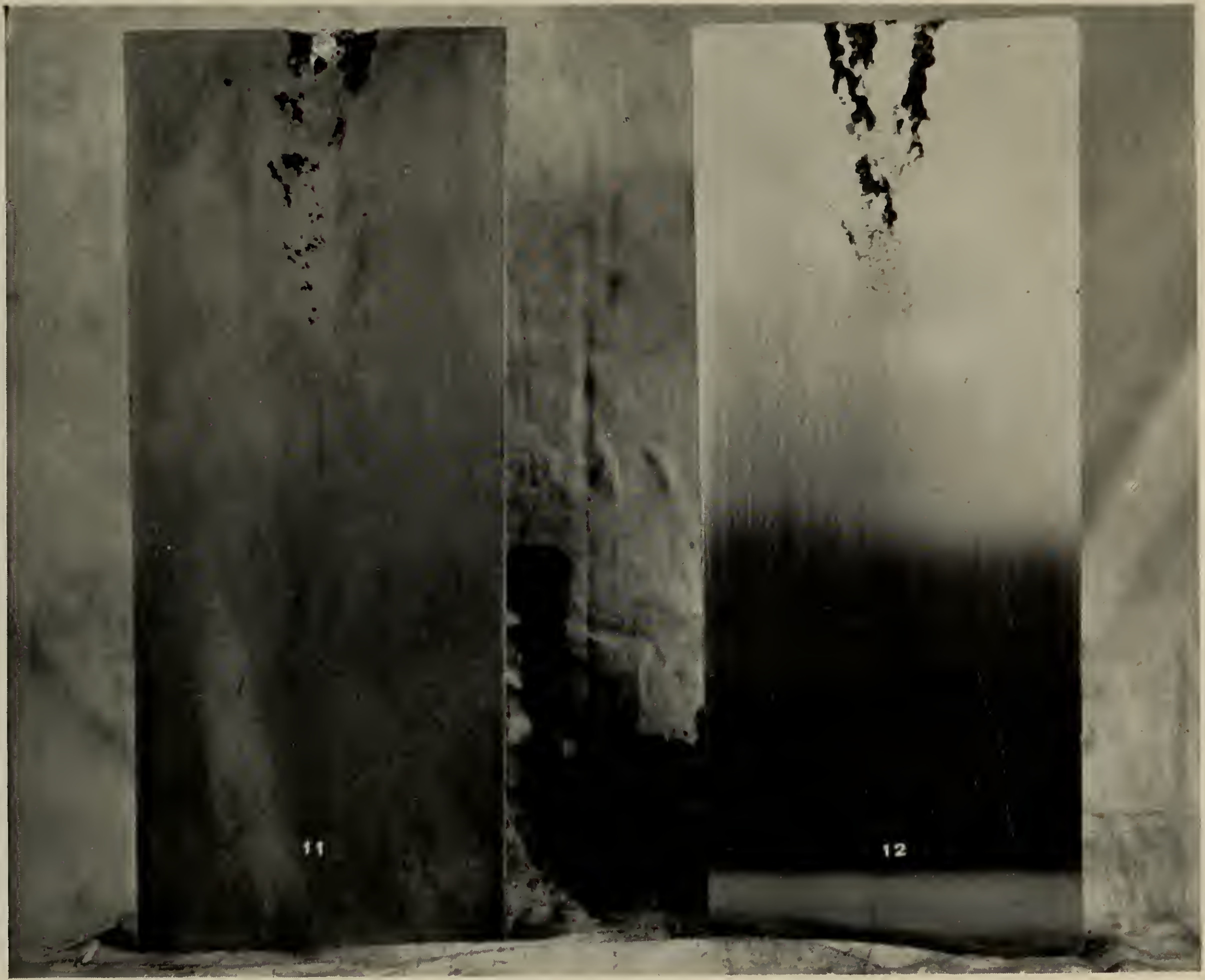

Fig. 5.—Ingots 11 and 12. Exper. 2. Steel made with about 0·40% Si in form of 50% ferro-silicon. Ingot 11 etched with iodine.

PLATE XVI

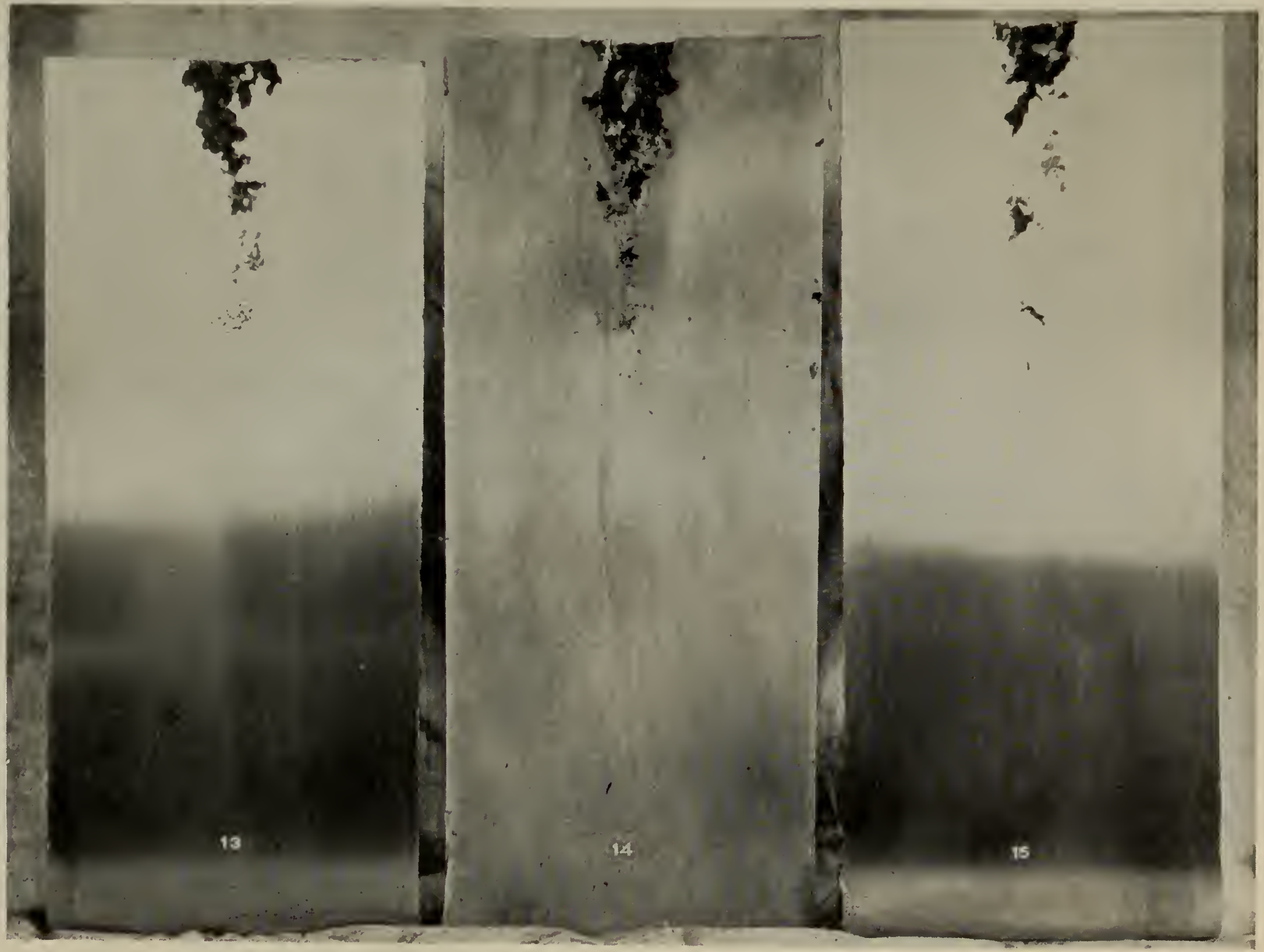

Fig. 6.—Ingots 13, 14 and 15. Exper. 2. Steel made with about 0·15% Al in form of 99% granulated aluminium. Vertical section. About one-third actual size. Ingot 14 etched with iodine.

PLATE XVII

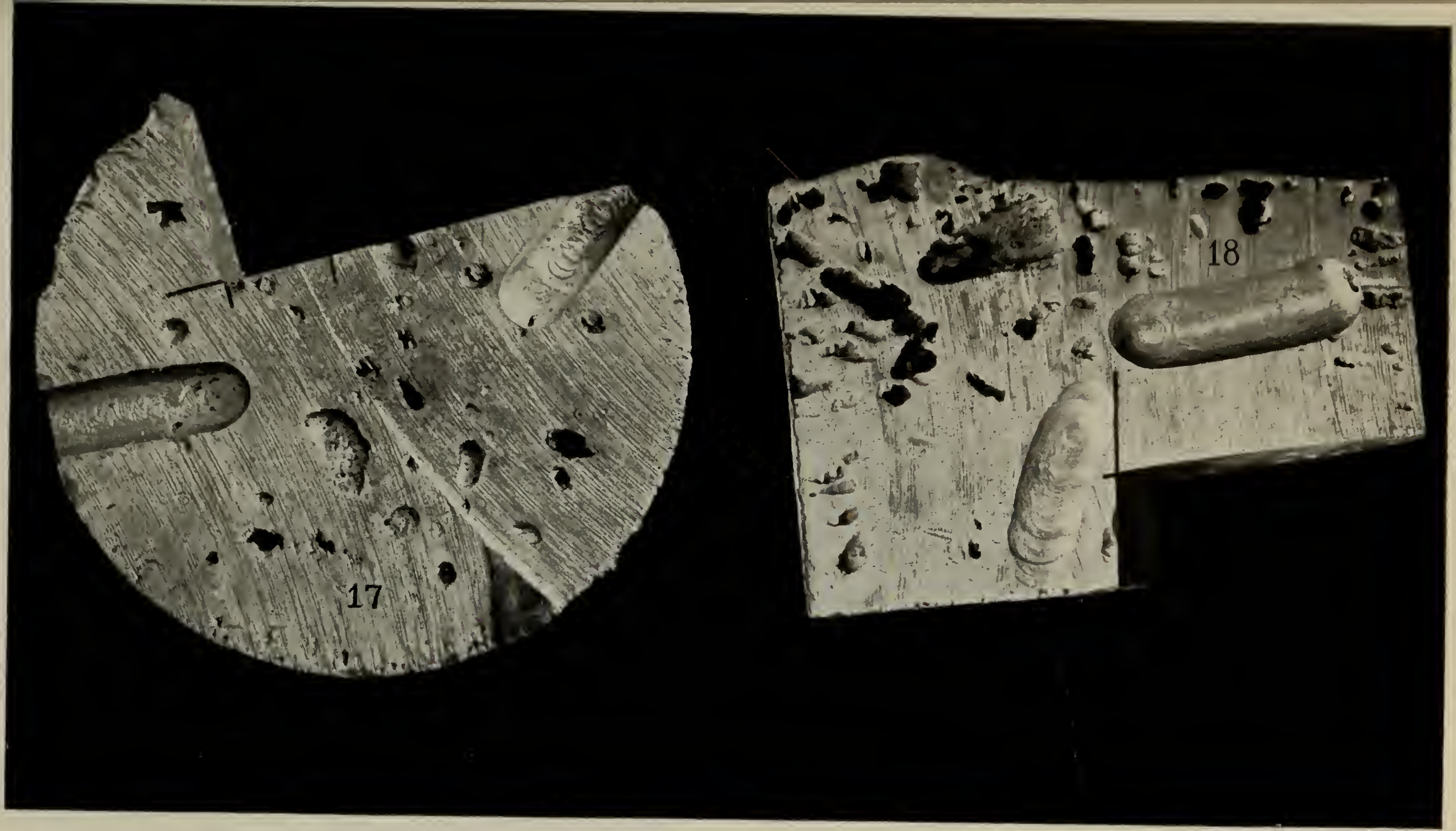

FIG. 7.—Ingot 17. Raw Converter Metal. Transverse Section. About two-thirds actual size.
Ingot 18. Same with ferro-manganese and ferro-silicon added but no deoxidizer. Vertical section. About two-thirds actual size.

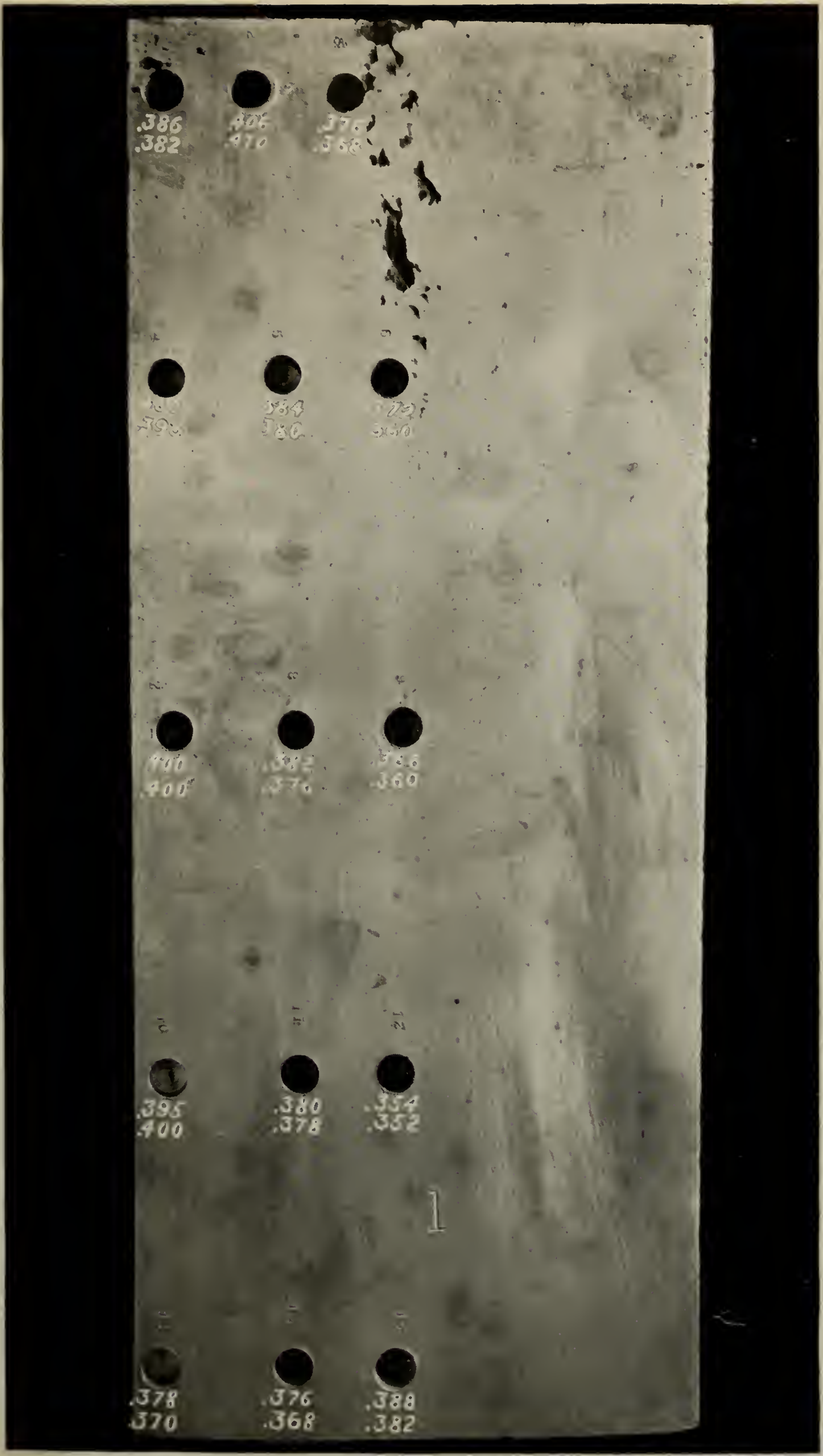
.386
.382
.406
.410
.384
.380
.400
.400
.382
.376
.360
.395
.400
.380
.378
.354
.352
1
.378
.370
.376
.368
.388
.382

Fig. 10.—Ingot 1. Exper. 2. Steel made with about 0·10% Ti in form of 15% ferro-carbon titanium with carbon determinations showing lack of segregation. Vertical section. About one-half actual size.

PLATE XIX

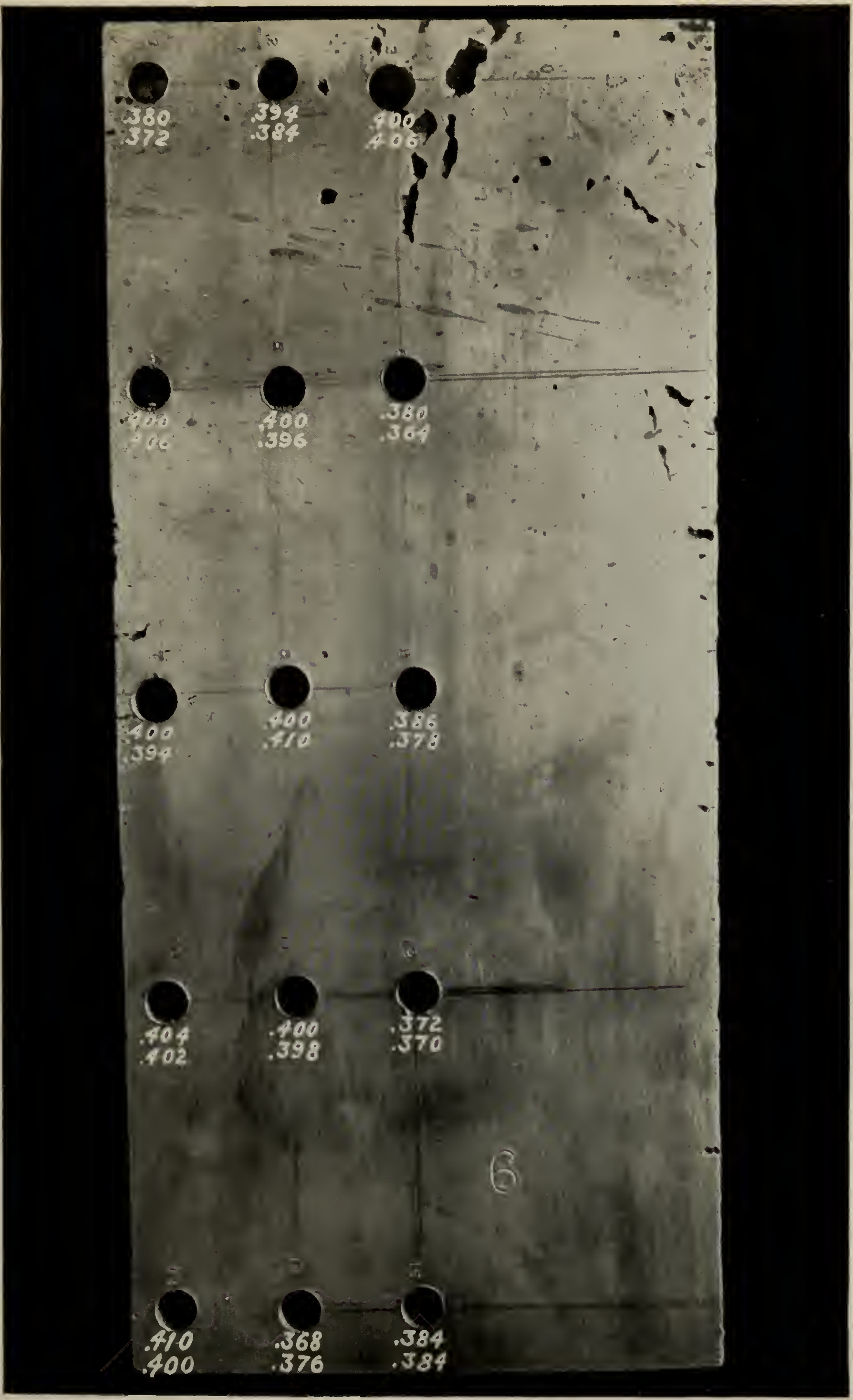
.380
.372
.394
.384
.400
.406
.400
.396
.380
.364
.400
.394
.400
.410
.386
.378
.404
.402
.400
.398
.372
.370
6
.410
.400
.368
.376
.384
.384

FIG. 11.—Ingot 6. Exper. 2. Steel made with about 0·50 Mn in form of 80% ferromanganese. Vertical sections with carbon determinations showing lack of segregation. About one-half actual size.

PLATE XX

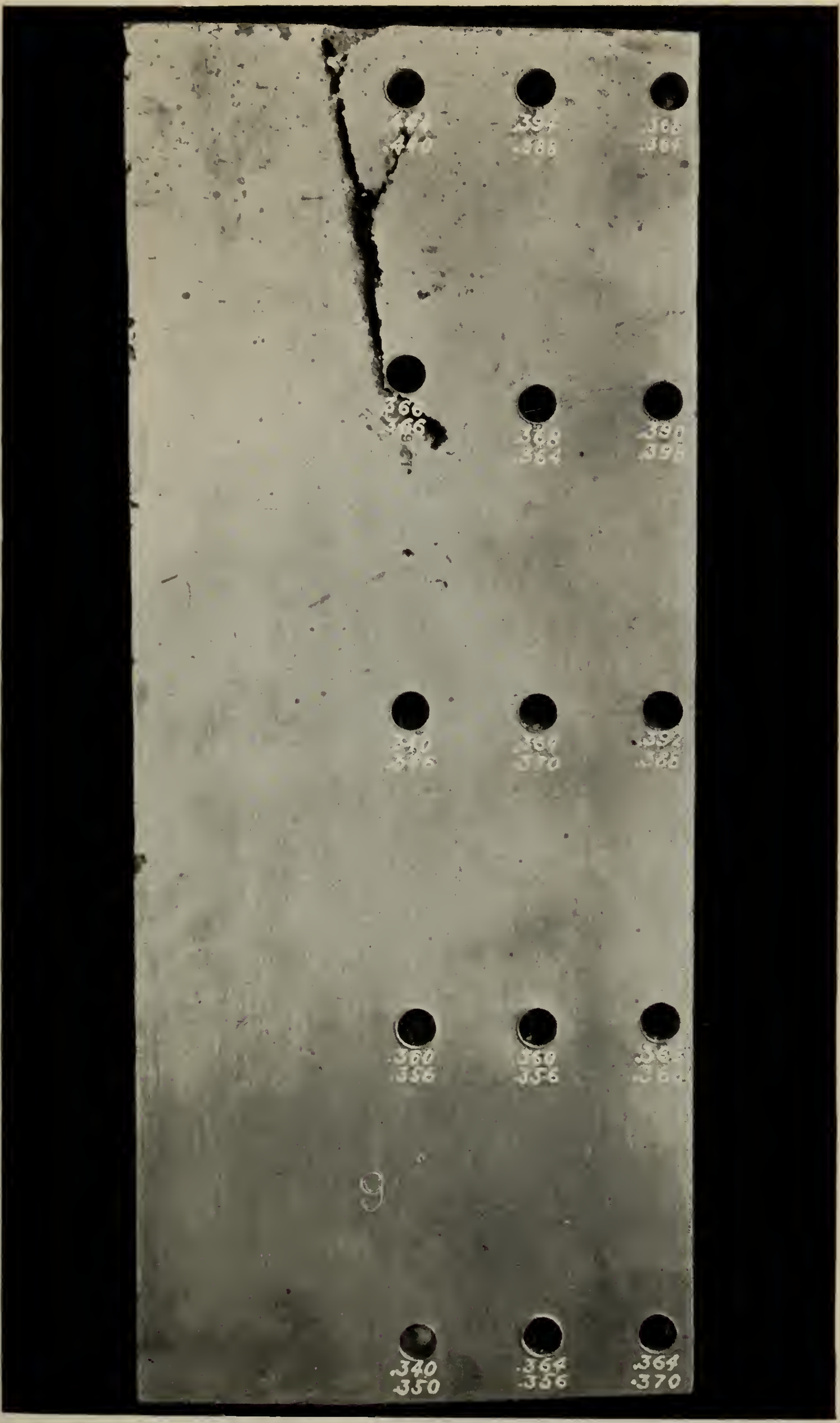
.366
.366
.360
.356
.360
.356
9
.340
.350
.364
.356
.364
.370

FIG. 12.—Ingot 9. Exper. 2. Steel made with about 0·10% Ti in form of 25% carbon-free ferro-titanium. Vertical sections with carbon determinations showing slight segregation near pipe. About one-half actual size.

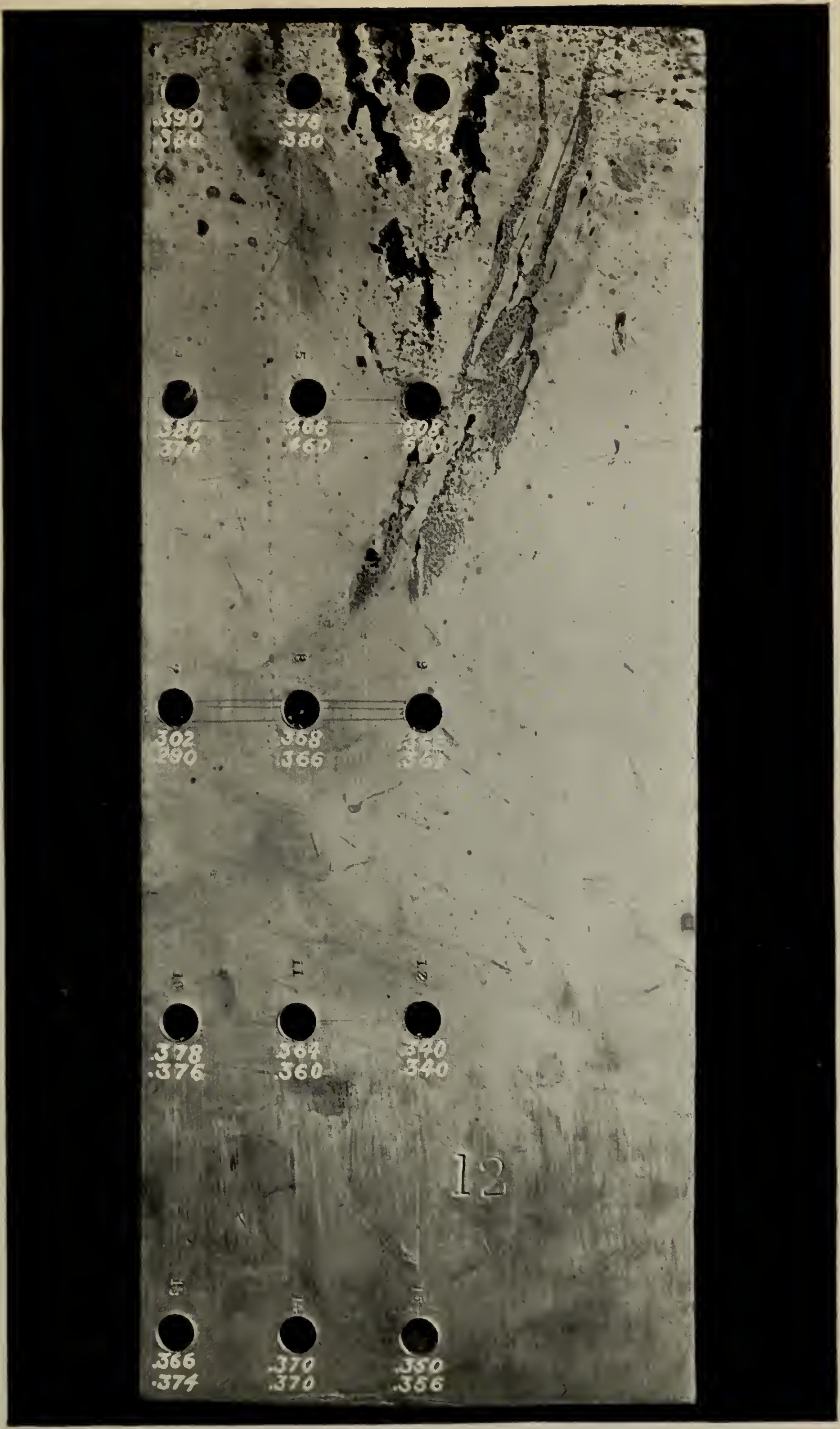
.390
.380
.378
.380
.374
.366
5
.380
.370
.466
.460
.608
7
8
9
302
290
368
366
11
12
.378
.376
.364
.360
.340
.340
12
15
.366
.374
.370
.370
.350
.356

FIG. 13.—Ingot 12. Exper. 2. Steel made with about 0·40% Si in the form of 50% ferro-silicon. Vertical section with carbon determinations showing approximately 60% segregation of carbon at drill hole. No. 6 located at the bottom of the pipe and about 30% from the top of the original ingot.

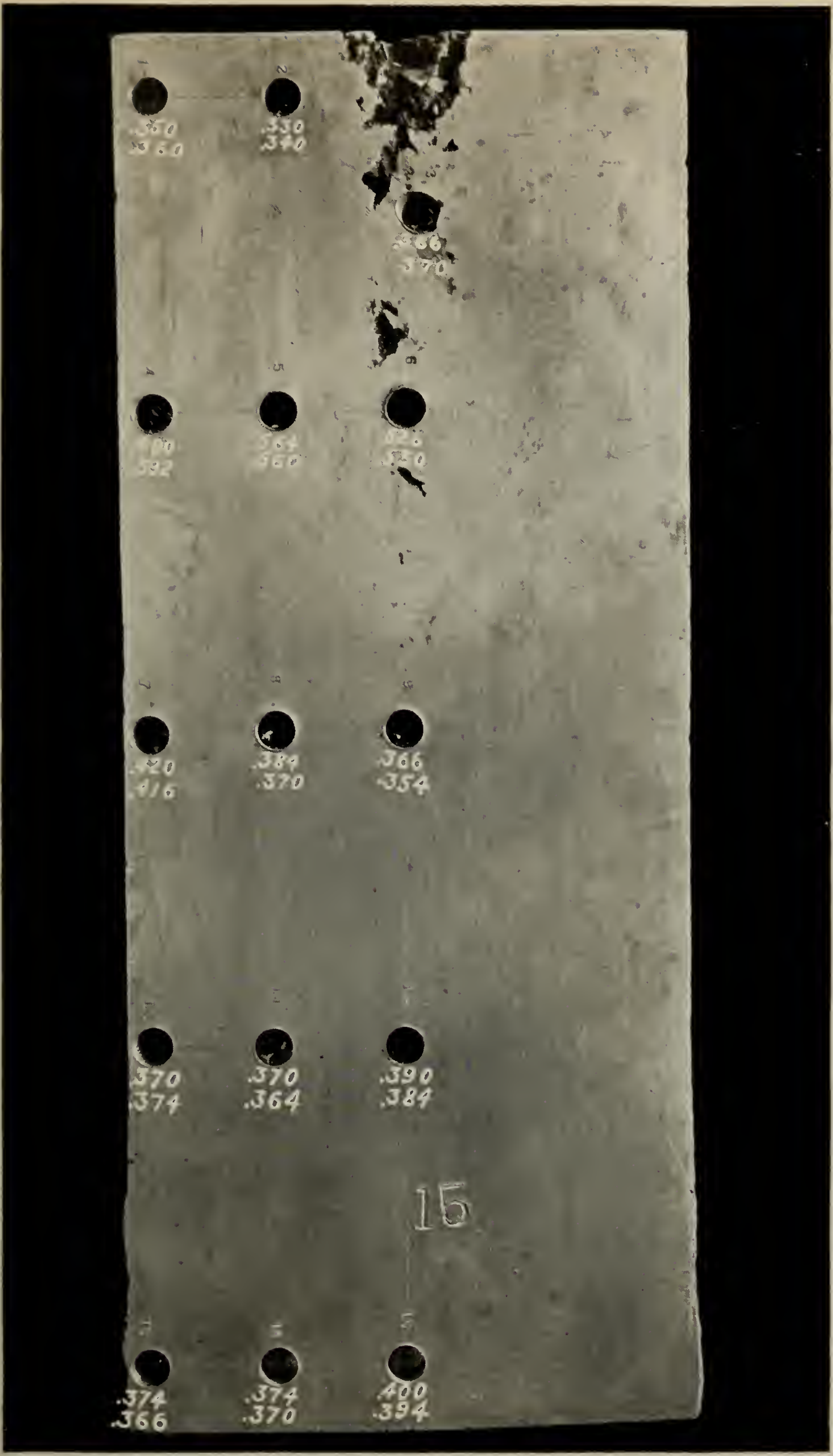
.330
.340
.366
.370
.364
.420
.416
.384
.370
.366
.354
.370
.374
.370
.364
.390
.384
15
.374
.366
.374
.370
.400
.394

FIG. 14.—Ingot 15. Exper. 2. Steel made with 0·15% Al. Vertical section with carbon determinations showing approximately 30% segregation of carbon at the bottom of the pipe and about 30% from the top of the original ingot. About one-half actual size.

PLATE XXIII

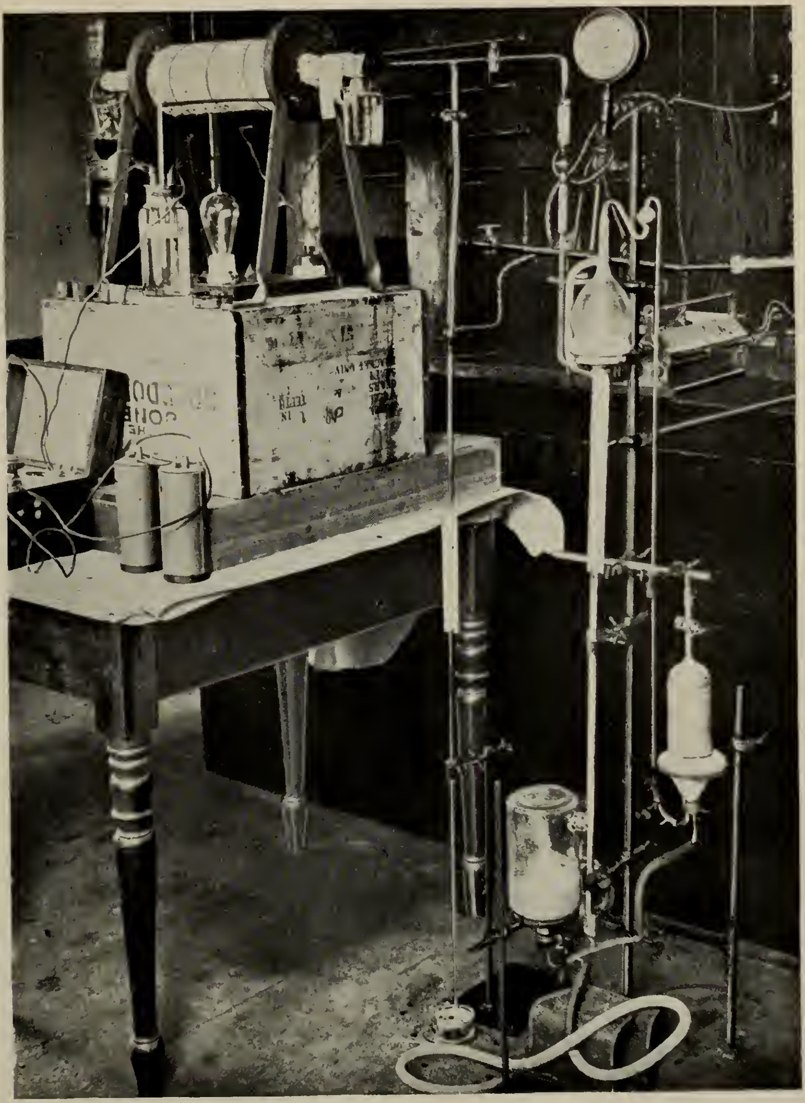

FIG. 16.—General arrangement of gas-extraction apparatus.

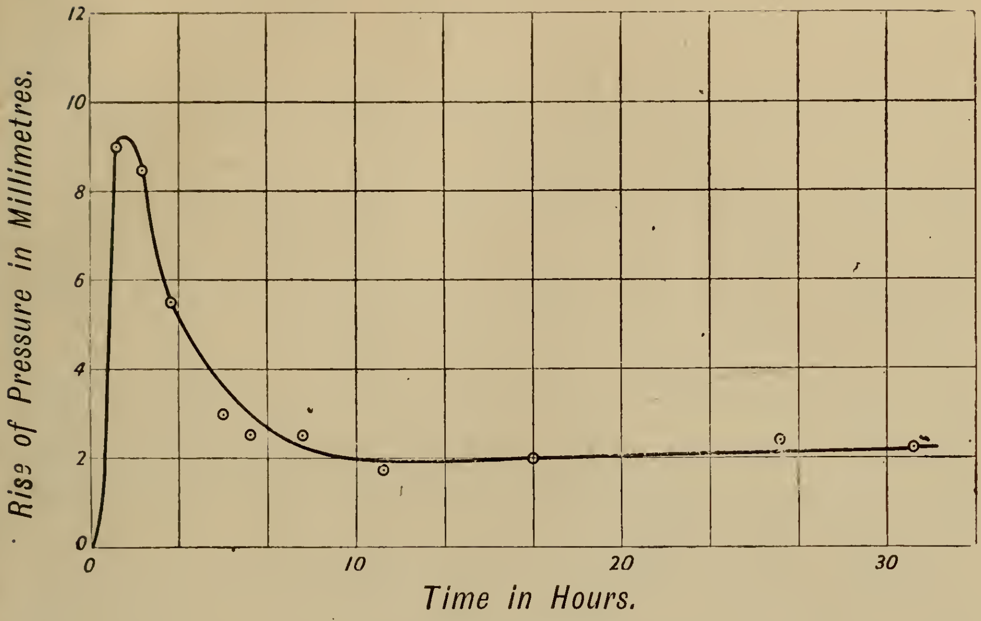

FIG. 24.—Sample 15. (Al.)

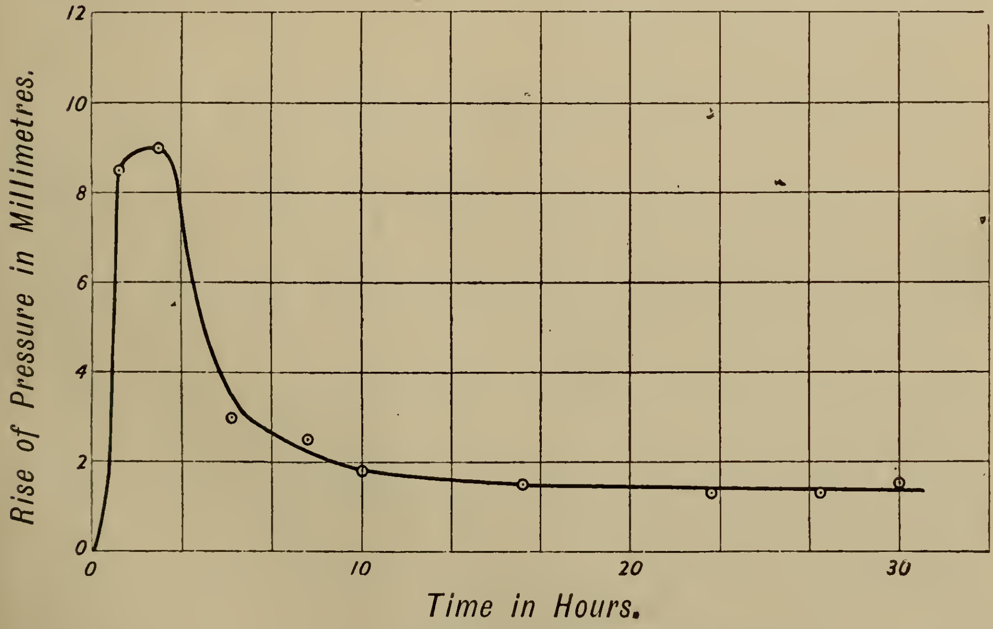

FIG. 25.—Sample 17-1. (Raw Converter Metal.)

45 ounces per ton of steel) is about one and a half times as much as the largest percentage of aluminium recommended by the manufacturer, although from Chart 1 (Fig. 17) of the first report it will be seen that 0·2 per cent. aluminium, which was the amount aimed for in Experiment 2, gave an average relative density of over 7·93. For silicon and manganese no recommendations could be obtained from the manufacturers, and proportions recommended by various metallurgists were used in Experiment 1, and the proportion giving the soundest ingots in that experiment was used in Experiment 2.

As in the preliminary experiments, the raw converter metal was comparatively free from blowholes (see Fig. 1, Part I., and Plate XVII., Part II.). All of the ingots in Experiment 2 except 17 and 18 were much sounder than those in Experiment 1, as might have been expected.

*Density.*—Both the density and the specific gravity tests were rather disappointing. To obtain good results in measurements of density it is believed that ingots must be weighed, either with the pipe left open or after cropping off the piped portion. In experiments like the present one, specific gravity tests from small specimens, unless taken from many places in the same ingot and averaged, are of little value.

*Tensile Tests.*—It will be noticed from Tables VII. and IX. that the order of the deoxidiser as regards tensile strength is exactly the same whether taken from the annealed cast metal or the annealed forged metal, although of course the actual strength figures are much higher in the forged material than in the cast condition. The elongation figures do not check so well, but again, as would be expected, those for the forged metal are much superior to those of the cast metal.

*Impact Tests.*—The annealed forged steel is also much more resistant to impact shocks than the annealed cast steel, but the relative order of the deoxidisers as regards the Charpy tests is almost diametrically opposite in the cast and forged material.

*Segregation.*—There is little doubt as to the proper order of the deoxidiser as regards its influence on carbon segregation so far as these tests went (see Table XII.).

*Gas Extraction Tests.*—Baker's results showing a large difference between the gases given off from steel with and without aluminium

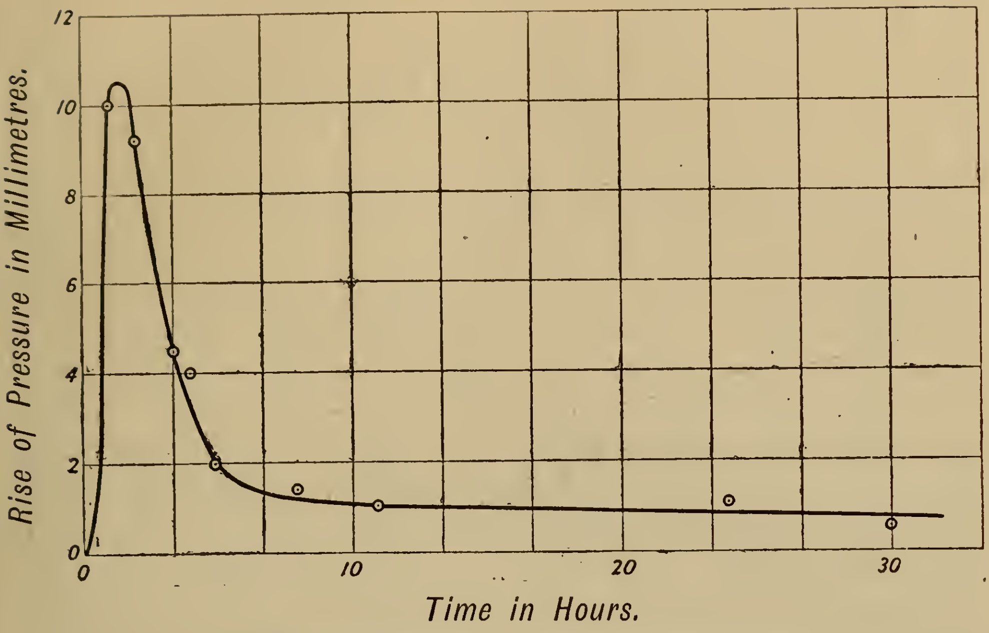

FIG. 26.—Sample 18-1. (Steel without Deoxidiser.)

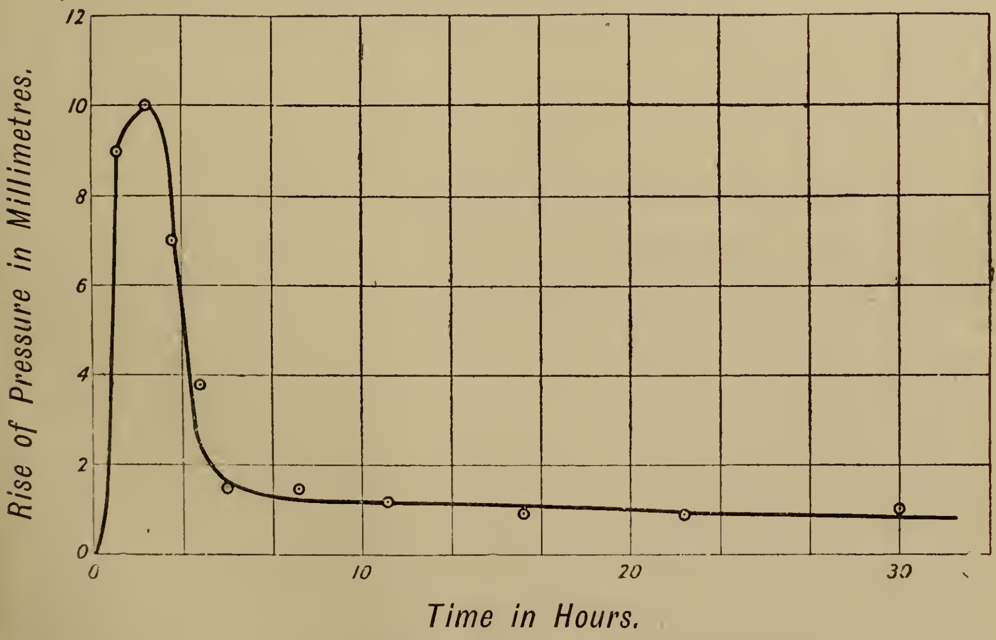

FIG. 27.—Sample 18-2. (Steel without Deoxidiser.)

were not checked in these experiments, although the conditions were somewhat different.

It is not entirely clear what relation the gas extraction tests bear to the present research. They form a valuable record as far as they go, but it is not clear that the steel which gives off the most gases in such a gas test as this is necessarily the most sound or the most unsound material. Practically all of the gas test-pieces in this experiment were sound on the outside at least, and the identical pieces used for the specific gravity tests (Table V.) were used in the gas tests, yet there is no direct relation shown between these two tests; for instance, the ingots cast with Fe.Ti. carbon-free gave the highest average specific gravity, while the samples with Fe.Mn. and Al. additions both gave out more gases. There are two cases where deoxidisers might affect the evolution of gases: (1) in the molten steel, and (2) in the steel during solidification. An ideal deoxidiser presumably would be one which would allow the maximum amount of gases to be given off from the molten steel while preventing such gases as remained in the steel from being given off during solidification. It is not clear that the tests which have been made are a measure of the influence of the deoxidisers in either of the above cases, for they give no information as to the relative amount of gases evolved from the molten steel and from the steel during solidification. The tests do show, however, that some of the deoxidisers, notably Fe.Mn. and Al., favour the retention in solid solution of such gases as remain in the steel after it has begun to solidify.

*Microscopic Examination.*—Preliminary microscopic examination was made from the tensile test specimens, which showed a considerable amount of slag present, as might have been expected from the small size of ingot used, and because no special precautions were taken in pouring to keep the slag out of the mould. The irregularity of the slag has doubtless affected the physical properties, and a great many more physical tests should be made from these ingots if valuable conclusions are to be drawn from them. It is hoped to make further microscopic examination with a view to throwing more light on the irregularity of the physical tests in Experiment 2, but the results will have to be published in a later report.

*Cost of Deoxidisers.*—The question of cost is of vital interest to the manufacturer. The following table (XXVIII.) will show the relative cost of the deoxidisers per ton of steel. The normal price of the deoxidisers rather than the war price is used, although the author realises that prices of ferro-manganese and aluminium have been almost tripled during 1915.

Table XXVIII.—*Calculation of Cost of Deoxidisers per Ton of Steel. Based on Experiment* 2.

| Deoxidiser. | Ounces Deoxidiser Used per Ton of Steel. See Table III. | Normal Price[1] of Deoxidiser. | Cost of Deoxidiser per Ton of Steel. |
|---|---|---|---|
| Fe.C.Ti. | 212 | \$0.10 per lb. | \$1.33 |
| Fe.Mn. | 198 | \$39.65 per ton. | 0.25 |
| Fe.Ti.(carbon-free) | 125 | \$0.30 per lb. | 2.31 |
| Fe.Si. | 229 | \$71.12 per ton. | 0.51 |
| Al. | 46 | \$0.19 per lb. | 0.55 |

*Density as Measured by the Number of Blowholes in Vertical Sections* (Plates XII. to XVI. inclusive).—Ignoring the pipe, the density as measured by the lack of blowholes in the vertical sections of the ingots gives the following order, No. 1 being the group of ingots most free from blowholes. In the same table is given the relative order of deoxidiser as regards influence on piping.

Table XXIX.—*Order of Deoxidisers as regards Soundness and Piping.*

| Deoxidiser. | Relative Order of Deoxidiser as regards Soundness. | Relative Order of Deoxidiser as regards Piping. |
|---|---|---|
| Fe.C.Ti. | 4 | 1[2] |
| Fe.Mn. | 5 | 4 |
| Fe.Ti. (carbon-free) | 3 | 5 |
| Fe.Si. | 2 | 2 |
| Al. | 1 | 3 |

---

[1] Since writing the above, the price of 80 per cent. ferro-manganese in the United States has advanced to \$350.00 per ton, while aluminium for steel-making purposes has advanced to sixty-five cents a pound. The two titanium alloys have apparently not advanced in price to any considerable extent. The market for 50 per cent. ferro-silicon is nominal. (March 10, 1916.)

[2] The group of ingots with the smallest pipe is designated as No. 1.

## CONCLUSIONS.

It was not to be expected that any very startling difference would be noticed in the action of the deoxidisers tested. If there were such a difference, it is reasonable to suppose that manufacturers would be more unanimous in choosing one or more of them to the exclusion of the others.

The evidence obtained in these experiments, either on account of the small number of tests or because of experimental difficulties, is not conclusive, but the results of the various tests are collected below in Table XXX., and give a graphic idea of the influence of the deoxidisers tested. Their relative merits, however, depend so much on just what is sought in the steel that each manufacturer must decide for himself which deoxidiser will best suit his needs.

TABLE XXX.—*Relative Order of Deoxidisers as regards their Various Influences.*

| Order of Deoxidiser with regard to Influence on | Fe.C.Ti. | Fe.Mn. | Fe.Ti. Carbon-free. | Fe.Si. | Al. |
|---|---|---|---|---|---|
| Density (Table IV.) | 1 | 5 | 2 | 4 | 3 |
| Specific gravity (Table V.) | 2½ | 4 | 1 | 5 | 2½ |
| Soundness (Table XXIX.) | 4 | 5 | 3 | 2 | 1 |
| Piping (Table XXIX.) | 1 | 4 | 5 | 2 | 3 |
| Tensile strength, cast condition (Table VII.) | 2 | 3 | 4 | 1 | 5 |
| Elongation, cast condition (Table VII.) | 1 | 3 | 5 | 2 | 4 |
| Tensile strength, forged condition (Table IX.) | 2 | 3 | 4 | 1 | 5 |
| Elongation, forged condition (Table IX.) | 4 | 5 | 2 | 3 | 1 |
| Charpy test, cast condition (Table X.) | 2 | 3 | 5 | 1 | 4 |
| Charpy test, forged condition (Table XI.) | 5 | 3 | 2 | 4 | 1 |
| Carbon segregation (Table XII.) | 2 | 1 | 3 | 5 | 4 |
| Cost of deoxidiser per ton of steel (Table XXVIII.) | 4 | 1 | 5 | 2 | 3 |

For a direct comparison of the density and the specific gravity, the results given in Tables IV. and V. are repeated below in Table XXXI., together with the mean of the two figures.

TABLE XXXI.—*Experiment 2. Comparison of Density and Specific Gravity Figures.*

| | Fe.C.Ti. | Fe.Mn. | Fe.Ti. Carbon-free. | Fe.Si. | Al. |
|---|---|---|---|---|---|
| Relative density (Table IV.) | 7·85 | 7·76 | 7·82 | 7·77 | 7·79 |
| Specific gravity (Table V.) | 7·769 | 7·753 | 7·773 | 7·746 | 7·769 |
| Mean | 7·81 | 7·757 | 7·79 | 7·758 | 7·78 |

The author realises that although the amount of work done in these experiments was great, there is still more work to be performed. With the data in hand the question of the relative merits of these deoxidisers cannot be definitely decided. He hopes, however, that this collection of data will be useful as far as they go, and that it will inspire others to continue investigations along the same lines, preferably with larger ingots.

In conclusion, the author wishes to express his deep appreciation of the many courtesies extended to him by Colonel Wheeler, commanding Watertown Arsenal, where all the foundry work and most of the physical tests were performed. Major Williams, Major Wesson, and Mr. Brown gave valuable assistance and advice in regard to the foundry work. Captain J. J. Thomas especially, by his advice and suggestions and his assistance in administering the details of mechanical arrangements, has added much to the value of these rather difficult and complicated experiments. Mr. Nead, Metallurgist, and Mr. MacNutt, Chemist, at the Watertown Arsenal, also gave valuable assistance. The specific gravity tests and the gas extraction tests were performed under the author's direction by Dr. F. C. Langenberg in the metallurgical laboratories of Harvard University. Professor Albert Sauveur has been consulted on each important step in the work. Some of the work, including the microscopic examination, was performed in the laboratories of Sauveur and Boylston.

# DETERIORATION OF REFRACTORY MATERIALS,

## WITH SPECIAL REFERENCE TO OPEN-HEARTH PRACTICE.

By H. B. CRONSHAW, B.A., Ph.D., A.R.S.M.

## PART II.

## OPEN-HEARTH FURNACES.

A further consideration of the difficulties involved in connection with the rapid destruction of open-hearth furnaces, particularly the roof and regenerators, has strengthened the conclusion previously arrived at,[1] namely, that the principal cause of the evil is to be found in the fluxing action of the dust. Further, that this dust, so troublesome in the regenerators, is in the main composed of ferric oxide and lime in the case of basic furnaces, and that it is chiefly derived from the charges. It is also probable that some of the loose dust which collects on the upper surfaces of the regenerator-bricks is carried backwards and forwards through the furnace between the two sets of regenerators, thus materially assisting in the wearing away of the roof.

It is widely realised that any practical solution of the difficulty would effect a considerable economy of time, labour, and expense. In the case of the particular furnace we are dealing with at this point, the two most vulnerable parts which call for immediate attention are the regenerators and roof. These will be considered separately below.

### I. The Regenerators.

It was previously pointed out, in a discussion on remedies, that two alternatives present themselves;[2] the first consists in removing the dust before it actually enters the chequer-work, and the second depends on selecting bricks capable of resisting the chemical activity of the dust, supposing it is allowed to invade the chequer-work. The former of these will be first considered. It also offers two alternatives.

---

[1] *Iron and Steel Institute: Carnegie Scholarship Memoirs*, 1915, vol. vii. Part I, pp. 18–40.

[2] *Ibid.*, p. 39.

The question at once arises as to what particular stage in the career of the dust would there be the greatest chance of effecting its capture. For instance, it is conceivable that the simplest and most direct way would be to prevent any dust from entering the furnace; that is, to remove it from the charges, previous to the operation of charging. This, for example, might involve a preliminary process of transforming all finely divided material into a coarsely granular condition. There is, of course, the fact that it would be a most difficult matter to free the charges entirely from dust, on account of the friable nature of the lime and limestone, even in the condition of lumps. However, it would seem quite possible to eliminate the greater part of the dust by mixing the charges with a harmless binding material and then burning. By some such process as this the material would be reduced to a coarsely granular and lumpy condition. It would also seem possible to find other means for removing the dust before actually charging the materials into the furnace.

However, in place of any preliminary treatment of the charges it might be considered more expedient to effect a capture of the dust at a later stage; say, within the slag-chamber, before it can enter the chequers. To carry out any proposal of this kind would involve either building regenerators on an entirely new plan, or else bringing about certain modifications in those at present existing. Several forms of arrangement might be suggested, but in view of the ready adaptability to modification of those already existing, it has seemed advisable to offer, for practical consideration, one form, diagrammatically shown in Fig. 1, and explained more fully below.

The slag-chambers, as they exist at present, naturally remove a great deal of material which would otherwise increase the trouble in the chequer-work. However, the material retained at this point consists only of the coarser portions, and all the dust passes at once into the chequer-work. Since the gases in most cases enter from above, the dust immediately collects in

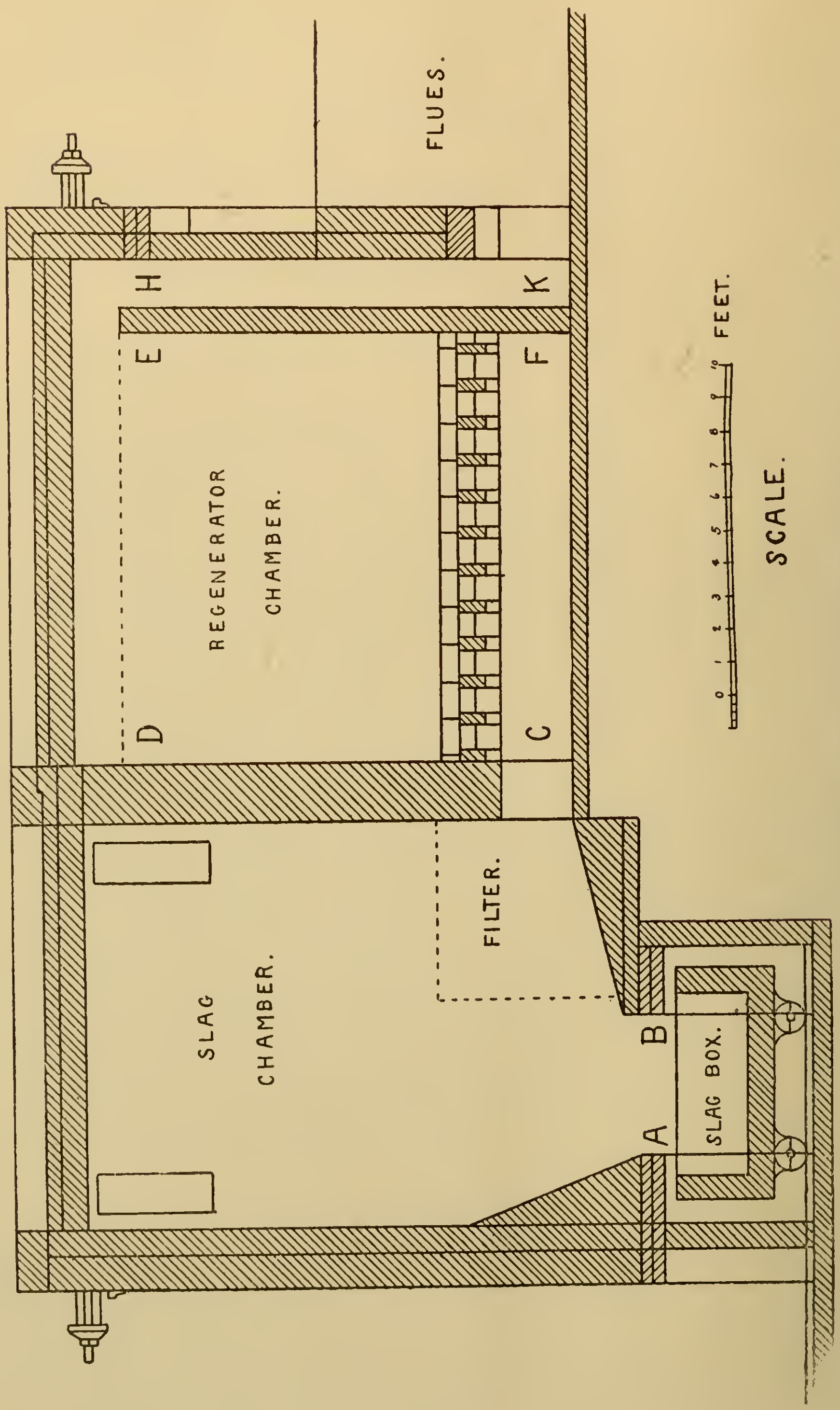
FLUES.
H
K
E
F
REGENERATOR
CHAMBER.
D
C
FEET.
0 1 2 3 4 5 6 7 8 9 10
SCALE.
FILTER.
SLAG
CHAMBER.
B
A
SLAG BOX.

Fig. 1.—An Improved Form of Regenerator.

the upper surfaces of the bricks. The effect of this can easily be seen by examining a chequer-work after a few weeks' use. The upper surfaces will be found to be heaped up with a dark red dust, which, at its contact with the bricks, is undergoing fluxation. Thus arises a viscous slag which slowly flows down the vertical faces of the chequer-bricks and collects on their under surfaces, forming small stalactites, from which it drips through the chequer-work. It is thus obvious that the destructive action is accumulative. If the gases entered from below this trouble would to a large extent doubtless be obviated. There is also the question of effecting a speedy removal of the slag which accumulates in the slag-chamber. In ordinary cases this usually involves a considerable expenditure of time and labour.

Fig. 1 indicates, in a more or less diagrammatic way, the result of certain alterations applied to one of the regenerators attached to a modern type of 40-ton basic open-hearth furnace. Here the slag-chamber would have to be deepened about 13 feet, and arches erected at A and B, at a height of about 5 feet above the floor. The inner part of the arch A would have to be built upon so as to form an inward sloping wall. Between B and the dividing-wall there is a similar, but stepped, piece of brickwork. This latter constitutes the foundation for the "filter," which consists of a chequer-work of bricks, arranged so as to present to the dust particles swept along by the gases as many points of contact as possible. Furthermore, the bricks chosen for the "filter" should be highly siliceous, yet capable of surface fusion at not too high a temperature. The lowest bricks of the "filter" are built into the stepped brickwork so as to afford a sound base for the superstructure, and in addition, are arranged so as to leave adequate passages for accumulations of slag. The opening in the upper part of the dividing-wall DC is built up, and the connection made at C in the lower part. There is no question but that a decided advantage would be gained by replacing the usual type of chequer-work by an arrangement which presents a smaller area of directly opposing surface to the inflowing gases; for it is upon these upper and lower surfaces of the bricks, placed as they are at right angles to the direction of movement of the dust-particles, that most of the finely divided matter is caught. One way of avoiding this difficulty would be to divide up the chamber into vertical hexagonal air-spaces by honeycomb-bricks. This is done for the whole space available, up to the line DE, and as far forward as EF, where a down-take has to be provided for. Here a wall EF is built up, or else a space unoccupied by hexagonal bricks is left free. Thus the position of the connection with the flues remains unaltered. With reference to the necessity of devising some means of quickly removing the slag from the slag-chamber at certain intervals, the trench-like excavation is continued beyond the slag-chamber for a few yards, and upon the floor rails are laid down and continued into the chamber. They carry a movable "slag-box," consisting of a rectangular framework of wrought-iron or steel plates, lined with fire-bricks, and running on small wheels. When the "slag-box" is in position within the slag-chamber, the lining of the latter projects well over the sides and ends of the former.

The question now arises as to what improvements in working may be looked for in the event of any such improved form of regenerator, as is here proposed, being adopted. In the first place the enlarging of the slag-chamber will certainly be a step in the right direction, in so far as increasing the settling tendency of the coarser material brought over by the gases is concerned. As the gases enter the "filter" they will be laden with the finer residuum of the suspended material. The duty of the "filter" is to extract most, if not all, of this material. The efficiency of the extraction process depends mainly on the arrangement of the bricks. Every particle must be given adequate opportunity of being impelled against the sticky surface of a brick, where it is retained to aid in the process of fluxation. As a result of this there will be a constant dripping of viscous slag from brick to brick through the "filter," from which it escapes by running down the inclined bed into the "slag-box." Possibly the slag may not flow sufficiently rapidly, in which case it would be a simple matter to increase its fluidity by throwing in some suitable flux. Again, it might be advisable to erect an arch with an inwardly inclined upper surface over the filter, so as to protect it from the effects of the coarse material. This would, of course, lengthen the life of filter-bricks. Thus, on emerging from the "filter," the gases would be deprived of the greater part of their load, and on entering the regenerator-chamber would pass upwards through the chequer-work. In this case whatever dust has escaped will be carried through the hexagonal passages, and only a very small portion of it will have the opportunity of coming in contact with the exposed bricks. Furthermore, if honeycomb-bricks are used, no facilities are offered for the accumulation of slag at any point, which is quite unlike the state of affairs existing in the usual chequer-work arrangement.

It has also been found possible to devise an alternative arrangement which dispenses with the somewhat cumbersome block. Once the initial cost is covered there is no doubt that it would prove a more efficient installation than the usual type of regenerator. By being in direct communication with the body of the furnace the block, in its usual massive form, is not required. The heat is utilised to much greater advantage, and the slag is employed as one means of retaining the dust. Furthermore, the regenerator proper can be readily opened up for inspection, or the "filter" and slag quickly removed, and a new "filter" immediately substituted. Likewise the whole structure could be readily replaced by another.

## II. The Roof.

The results of previous inquiry have shown that the rate of erosion of silica-bricks in the roof of a basic open-hearth furnace may be taken as being about $1\frac{1}{2}$ to 2 inches per week.[1] Apart from the relatively subsidiary effects of abrasion and volume-changes, there can be no doubt the main source of destruction is to be sought in fluxation; primarily due to the fine particles of dust from the solid charges, and to some extent from the producers and regenerators, and secondly to the volatilised substances like ferric oxide, arising from the bath of molten slag and metal. So long as fluxation is confined to the surface of the bricks the matter is not very serious, but it becomes so when cracks leading into the interior begin to develop. In any case, whether regularly or irregularly, a progressive advance must take place. On the outer portions slag is formed, but as soon as it collects in any quantity, it is swept away by the force of the incoming gases. Thus two processes go on hand in hand; the supply of fine basic particles for fluxing purposes, and the constant removal of the slag, thereby exposing fresh surfaces for attack. It would appear, therefore, that the degree of permeability is not so important a quality as might at first sight be supposed, and this is also borne out by actual examination of used bricks, together with various micro-sections cut from them, as already described. There was nearly always a sharp line of demarcation between the thin layer of slag and the recrystallised zone adjacent to it, and although this particular zone, A in Fig. 1, Plate V., of the previous report was full of visible pore-spaces, and was also in a comparatively friable condition, yet there was no evident tendency on the part of the slag to penetrate into it. The layer of slag was always thin, and sharply marked off from the light grey band by an even plane, except where cracks had developed. Such phenomena may be explained by the fact that the slag is not allowed to accumulate in any quantity. Besides this there is also the possibility of the pore-spaces being cut off from one another by impervious walls, that is, whilst the brick is exposed to the high temperatures of the furnaces, for this is not necessarily the case when the brick has cooled down to normal temperatures. In other words, the degree of permeability is low, although the actual porosity may be high. Apart from fluxation, considerable danger lies in the development of cracks, the weakening of joints, and the breaking away of pieces of the bricks. Abundant evidence of this can always be found on examination of a furnace-roof after it has been in use some time.

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[1] *Iron and Steel Institute: Carnegie Scholarship Memoirs*, 1915, vol. vii. Part I. pp. 22–25.

Just as in the case of the regenerators there are two ways of rectifying this wear and tear of the roof-bricks, that is, after internal cracking and erosion along the joints have been reduced to a minimum; either by removing the dust responsible for the fluxing effects, or by substituting neutral or basic bricks for the ones now in general use. As regards the first, reference must be made to the remarks made in connection with regenerators, as the same apply also to this case. The problem of manufacturing cheap and efficient basic and neutral bricks from natural deposits occurring close at hand, opens up a wide field for lucrative research. With the changed conditions that exist at the present time, the question has become even more vital, and there is no doubt that desirable results would be obtained at the cost of systematic and experimental investigation. There are mineral deposits in this country, for example dolomite, magnesian-limestone, limestone, serpentine, kaolin, and bauxite, which might be turned to very great advantage in this respect. There are difficulties, such as in the case of limestone, but these difficulties are by no means insurmountable. The degree of permeability, which would not be a factor of importance in the case of basic roof-bricks, requires consideration in the event of using such bricks for regenerators, thereby fulfilling the second alternative mentioned above. In both cases, however, any tendency on the part of the bricks to crack is a very serious matter indeed.

## BLAST-FURNACES.

In any discussion on refractories as applied to blast-furnaces, it is both customary and convenient to direct independent attention to the special requirements of the hearth, bosh, and shaft respectively; but before this plan is followed out here it will be well to consider a matter which affects every part of the furnace-lining alike. This is the question of the prevailing irregularity in names, sizes, and shapes of bricks. It is fully realised that the joints are the weakest parts of the brickwork, and a reduction of all such vulnerable points depends entirely on the efficiency of the brick-laying, which in turn depends to a very large extent on the uniformity in dimensions and shape of the bricks themselves. It is therefore useless explicitly to demand bricks of highly developed special qualities until the masonry has reached a sufficiently high standard of excellence.

The bricks designed for each particular part of the furnace ought to be correspondingly named in a proper manner, that is, stamped by the manufacturer with a standardised mark, so as to avoid any confusion in ordering and laying. This applies more particularly to special bricks of a tapered or unusual form. It is, of course, important that there should be general agreement amongst manufacturers on this point. It has even been recommended that the words "hearth," "bosh," "inwall," or "top" should be stamped on the brick, and in the case of special bricks, also their number and name. If this plan were universally adopted it would have the immediate effect of improving workmanship, economising labour, and obtaining a more highly resistant lining.

In connection with open-hearth furnaces the irregularity in dimensions has already been referred to as a serious matter waiting to be put in order. The same applies to blast-furnaces also. In most cases it must be due to carelessness of manufacture, and unremonstrative acceptance on the part of the furnaceman. Irregularity of size means increased cost of labour in obtaining anything approaching a satisfactory lining. At the same time there is necessarily a reduction in its term of life. The cost of lining a furnace with irregular bricks must be much greater than when equi-dimensioned ones are used ; the amount of mortar is considerably increased, as is likewise the time required for choosing and trimming.

These remarks similarly apply to irregularities of shape, due to warping. This can also be avoided if proper attention is given to obtaining a strictly uniform mixture, and by carefully regulating drying and burning.

Once the brickwork is completed, and the process of drying brought to a successful conclusion, and when the furnace has entered upon its customary duties, the lining comes under the influence of a number of agencies which work to bring about its ultimate destruction. Some idea of the various factors concerned in this may be gained by briefly describing an example, in the form of a furnace which was examined after it had been in action for a period of some thirty-eight years. From a point 13 feet below the top of the furnace down as far as the top of the bosh a thickness of about 2 feet 3 inches of brickwork had been removed. The carbonaceous "scar" began to be formed at a depth of about 28 feet, and continued downwards. Within the bosh the original thickness of the lining was preserved, although to a large extent replaced by the "scar." At the top of the bosh the "scar" graded into the brickwork in a manner which strongly suggested a process of gradual replacement. Behind the "scar" the bricks had suffered surprisingly little alteration. There were no signs of fusion or fluxation. A striking feature, however, was the extensive fissuring, both within the bricks themselves and between the various layers. These cracks and cavities were lined with small yellow hexagonal crystals of zincite, and a sample collected at a point about 35 feet below the top gave, on analysis, some 99 per cent. of zinc oxide and 1 per cent. of lead oxide. This may quite well indicate the presence of massicot, a naturally occurring oxide of lead which is sometimes found in furnace-products, or may possibly represent an isomorphous mixture of zinc and lead oxides. The crystals had entered into the most minute crevices, and were even present within the very pores of the bricks. No doubt this greatly aided in the general process of disintegration. On the authority of those engaged in pulling down the lining, these deposits of zincite were first encountered in abundance about 35 feet down, whilst at various points below a depth of 20 feet a good deal of white, powdery, and deliquescent zinc chloride is said to have made its appearance. Besides these minerals, others were collected which have not as yet been fully investigated. In any case, the entrance of these volatile bodies, in company with carbon, into the pores and crevices of the brickwork, and their subsequent crystallisation, are factors which clearly aid in the general process of destruction.

Returning now to more general considerations, yet confining our attention to the special parts of a furnace, we find that, in the first instance, the bricks used for the top must obviously be both tough and hard, in order to withstand the effects of impact and abrasion, necessarily arising when material is charged into the furnace. In some cases the wear and tear is diminished by the introduction of cast-iron "wearing-rings."

There is no doubt that erosion reaches its maximum in the shaft. The example previously cited is a case in point. As regards American practice, Diehl is of the opinion that failure in the shaft is responsible for 90 per cent. of the furnaces which are blown out. There appear to be two main destructive influences at work. The first is the deposition of carbon within the bricks themselves, and the second the deposition of certain volatile substances in the cavities and crevices running through the brickwork. The former mainly depends on the permeability and purity of the brick as regards active compounds of iron.

The deposition of carbon within the pore-spaces, and the secondary actions which follow, must have a very detrimental effect, so far as the coherence of the bricks is concerned. The process of substitution seems to advance progressively outwards, and since the "scar" is of a more friable nature than the original bricks, it falls a ready victim both to the abrasive action of the descending charges, and to local scaffolding. The latter is of course aided by the vertical nature of the sides, in contradistinction to the state of affairs which exists in the bosh. Thus substitution and abrasion work hand in hand. The second factor, that of volatilisation and deposition, affects that part of the brickwork between the "scar" and the outer shell. The very fact that crystallisation of volatilised compounds takes place here demonstrates the protective influence of the "scar," in so far as the conduction of heat is concerned. This is also borne out by the results of various investigations, which indicate that the most active decomposition of carbon monoxide takes place between 300° and 500° C. Amongst the deposits which have been observed may be instanced soda, potash, oxides of lead and zinc, and probably chlorides of zinc, sodium, and ammonium. The destructive action of these substances is not altogether confined to simple processes of disruption. In certain cases at least, say where local heating through irregular filling or any other cause takes place, secondary interactions between the constituents of the bricks and the adventitious minerals must take place. Quartz is a mineral liable to attacks of this kind, giving rise, for example, to alkaline silicates. It appears, therefore, that the inner zone of "scar" is in one sense protective, and in another destructive. It protects the more or less unaltered brickwork from the high temperatures of the interior and the fluxing influence of the charges, but at the same time it gives rise to conditions which favour the deposition of volatile compounds, capable of bringing about disastrous secondary changes, and moreover constitutes in itself a source of progressive and effective destruction, arising from the relatively friable nature of the substituted "scar." Therefore what is required in the first place is a brick entirely free from ferruginous impurities, and one having the minimum of permeability combined with sufficient resistance to internal fissuring. Furthermore, it must be sufficiently refractory to withstand the chance irregularities of overheating.

Within the bosh the formation of "scar" takes place to a still greater extent. The original thickness of the lining is, however, in many cases preserved, probably owing to the diminished influence of abrasion and scaffolding. The "scar" is consequently protective rather than destructive. If it is thought desirable to prevent these changes taking place, impervious and pure bricks must be used. Furthermore they should be of large size, so as to diminish the number of joints, and also chemically inert to the particular slag which is being formed. In view of the facts that the effects of abrasion and scaffolding are not felt to anything like the extent experienced in the shaft, and that in the bosh chemical activity becomes an important factor, it might, in some cases at least, be advisable to permit the formation of "scar" by using the ordinary bricks, and to back them with a few courses of non-ferruginous bricks set closely together, and of a kind not liable to undergo any fissuring. In other words, no opportunity must be given for the entrance of the volatilised products to any portion of the brickwork behind the "scar."

For the hearth impervious bricks of large size are required, and what is important, they should also be chemically inert to the usual type of slag which is formed, although the insertion of cooling devices allays this trouble considerably. The molten iron and slag have an extremely penetrating influence, and therefore all possible means of access should be avoided. In this respect it is important to reduce the permeability so far as is consistent with obtaining a high resistance to fluctuations in temperature, which are fortunately not so serious in character as those obtaining in open-hearth furnaces. The size and arrangement of the joints also require close attention.

## CUPOLAS.

There are very many types of cupolas, but from our point of view, the conditions to which their linings are subjected are more or less uniform for all cases. The working conditions in a particular example may be cited by way of illustration. The interior was lined with "best fire-bricks"; in the hearth from 3 to 9 inches in thickness, and in the shaft 4½ inches. The working period was from 5 A.M. to 5 P.M., during which time tapping was carried on at frequent intervals. The temperature of the metal during tapping may be about 1200° C., and that of the melting zone from about 1400° C. to 1800° C. The hearth and bosh required total relining every six to nine months, whilst the shaft survived two to three years. Fettling with ganister-mortar had to be carried out every day, and also at the week-ends.

Within the hearth the destructive influences at work are much the same as in the case of the blast-furnace, and the remarks previously made in this connection apply equally well to cupolas. In addition, it is important to note that the occasional oxidation of the iron, brought about by the use of insufficient coke, or too much blast, may accelerate the rate of erosion by fluxing the bricks. Another difficulty often arises by the clinging of the slag to the sides of the hearth, which necessitates its being broken off afterwards. When the metal is being tapped the layer of slag sinks, and is consequently brought into contact with a large part of the brickwork.

Within the bosh a noteworthy source of trouble lies in the local cooling effect of the incoming blast, so that iron may solidify, forming "scars," which cause serious damage to the brickwork on being subsequently removed.

A good deal of the wear and tear in the shaft is due to careless charging, when lumps of pig and scrap iron are thrown against the opposite side.

Thus the shaft-bricks should be tough and hard, the bosh-bricks tough, impervious, and refractory, whilst the hearth-bricks, besides being impervious and refractory, should be chemically inert towards the prevailing type of slag.

## STANDARDISATION.

It would appear, therefore, from a consideration of the above examples, that for each particular part of every variety of furnace, a lining of bricks possessed of certain definite chemical and physical properties is required. In other words, each portion of every furnace is characterised by certain actively destructive agents, of both a chemical and physical nature, so that in order to resist them effectively, corresponding properties are required in the bricks themselves. Thus, once these destructive agents are known, as well as their relative capacities, it then becomes a question of producing bricks of required qualities by regulating, first the composition and texture of the raw material, and secondly the details of the subsequent processes of manufacture. Purely empirical methods would in consequence give place to standardised processes controlled by strictly scientific principles. Some progress in this direction has already been made, the movement starting in January 1908, by the English Ceramic Society. It is encouraging to find that, as an outcome of this, the Refractory Material Committee of the Institution of Gas Engineers has framed a standard specification for the testing of retort and fire-brick material,[1] and it is to be hoped that a similar procedure will be extended so as to include the other industries, which depend so much on refractories. Standardisation of raw materials, finished products, and manufacturing processes is the first long step towards obtaining a systematic state of affairs to serve as a basis for future systematic improvements, and the time is now ripe for such a change to take place. In view, therefore, of its extreme importance, it has been thought advisable to draw attention to the main features involved in any consideration of the matter.

The various properties, both chemical and physical, which go to make up the quality of a raw material or finished fire-brick, ultimately depend on mineral composition and texture, so that a consideration of these will form a logically sound starting point, either for purposes of classification, or systematic research into the conditions which determine these properties. The method now in general use for classifying rocks depends partly on their mineral composition, and partly on their texture, thereby bringing together all those varieties possessing similar characteristics. For purposes of effecting a more thorough division, as in the case of fire-clays, where the texture is more or less uniform and the mineral composition difficult of determination, some other distinguishing feature must be made use of, such as softening point.

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[1] *Journal of Gas Lighting*, 1911, vol. cxiv. pp. 843–845.

[2] *Ibid.*, 1912, vol. cxviii. pp. 828–829.

*Mineral Composition.*—Bricks, and different kinds of raw material, consist of aggregates of minerals in the form of oxides, silicates, and other compounds. Therefore the kind, and relative amounts, of these constituents determine the chemical nature of the material or brick as a whole, that is, whether acid, intermediate, or basic in character, and in this respect also determine their chemical behaviour towards destructive agents, a matter which is obviously of first importance. The nature of the constituents, due regard being paid to their variety, relative amounts, and state of aggregation, will also largely influence the softening point, the volume changes, and other physical properties dependent on chemical constitution. However, the specific properties of any one mineral will be modified to a large extent by the presence of other minerals in the same aggregate; for instance a general lowering of melting points would be produced. When such an aggregate consisting of a variety of minerals is exposed to a rising temperature, progressive fusion takes place, the most fusible being the first to succumb, and from that point onwards a process of mutual solution takes place. The lowering of freezing points is the most characteristic feature of solutions, whether the constituents of these solutions be salts, metals, or silicates, oxides and other compounds. In rock-magmas it may happen that quartz, which alone melts at about 1600° C., first begins to crystallise out at a temperature of about 1100° to 1200° C. Lavas from Vesuvius have been observed to be still in a molten condition at a temperature of 1100° C. These observations are of course quite in accordance with the well-known physico-chemical laws of solution. It is therefore essential, in all cases, to have an exact idea of the mineral composition. This is best obtained by computation from reliable chemical analyses, and afterwards the results can be checked by examination of thin sections under the microscope. In this manner also, the presence of undesirable impurities, in both raw material and bricks, can be readily detected. Furthermore the microscope is especially useful in enabling one to follow the mineralogical changes which take place on burning, or subsequently using the bricks in industrial furnaces.

*Texture.*—This term refers to the manner of aggregation of the constituent particles, and also to the coarseness of grain of the aggregate. The particles may show all kinds of mutual relations as regards their state of aggregation. For example, they may be separated by a matrix, or placed in simple contact with one another, or intimately interlocked. In addition, the grain of the individual particles may vary from a large to an ultra-microscopic size. All these variations, included under "texture," have the greatest possible influence in the determination of the physical characteristics of raw material and finished products. It is of first importance, therefore, to have a reliable means of unravelling the texture of a body. This of course can only be done by cutting thin sections of the material in question, and subsequently examining them under the high powers of a petrological microscope, in both ordinary and polarised transmitted light ; just in the same way as rocks are studied, and their various mineral constituents and textures readily and quickly made out. In this respect alone the great value of the microscope cannot be too strongly emphasised. It is a curious fact, that although the microscope has found a useful application in metallurgy, particularly in connection with the manufacture of iron and steel, yet in all that concerns brick-manufacture it has, apparently, been totally neglected. This is in spite of the fact that in the latter case the conditions for its use are much more favourable, for here the constituents of the raw materials and finished products are generally transparent minerals with definite optical properties, so that a great deal of useful information can be obtained by their examination in transmitted polarised light, which is not the case with metals, where reflected light is in question. By this means the nature of all, except perhaps the most finely divided, mineral constituents can be easily determined. Likewise the mutual relations which these constituents bear to one another stand out clearly. One can estimate their relative sizes ; whether the material is coarse or fine grained, even grained or consisting of relatively large individuals embedded in a finely divided ground-mass. Besides this, one can see at a glance whether they are rounded, angular, or subangular, and how closely they are packed together, and in what manner. The larger individuals may be closely interlocked with only traces of matrix lying between, or they may be more or less loosely packed together with the interstices filled with matrix, or else, on the other hand, they may be sparingly scattered through a fine textured ground-mass. In this case it would be important to find out the nature of the large individuals, and likewise the composition of the ground-mass. Another point of moment is the internal structure of the individual grains themselves; whether much shattered, traversed by comparatively few cracks, or quite free from them. In addition to this the grains may enclose minute mineral inclusions, or cavities, whose identity can generally be made out by careful examination. Observations such as these, especially if correlated with the standardised tests described below, would go a long way towards helping one to form an opinion of a raw material for brick-making purposes, and it would be possible to foretell with a fair degree of accuracy the changes likely to take place on heating. Better than this the sample could actually be heated, the process arrested at various points, and the products sectioned and examined microscopically. The same applies to the bricks themselves, both during and subsequent to manufacture. One would then be able to follow the changes taking place at every stage, which is an all-important step towards gaining complete control over the various processes of manufacture.

Besides these what may be termed more indirect methods of estimating the various qualities of raw materials or fire-bricks, but which in addition to possessing the great advantage of cheap and ready application, provide a great deal of other useful information, there are various standardised tests which serve directly to measure these same qualities, that is in a comparative sense. They are, however, more strictly applicable to finished bricks rather than raw materials. These tests will be briefly considered below. The several physical properties which call for attention, but which naturally vary in relative importance according to the particular purpose for which the bricks are required, are: Softening point; permeability; resistance to temperature changes; dilatation; permanent expansion and contraction; hardness; toughness; crushing-strength. Besides these there is the question of uniformity in size, texture, and composition, and freedom from impurities, such as excessive amounts of iron compounds.

*Softening Point.*—This should be determined under strictly specified conditions, with special attention to the rate at which the temperature is raised. The most fusible and finely divided constituents will be the first to melt, and the remaining particles will then gradually succumb as the temperature rises, partly by mutual solution, partly by the formation of more fusible compounds as a result of chemical interaction, and partly by independent fusion. In the practical application of this test it is only possible to observe what may be termed the softening point of the test-piece as a whole; that is, when internal fusion has progressed to such an extent that the fragment loses its rigidity, and consequently begins to collapse. This is of course due to the fact that the material consists, not of one mineral alone, but of several, and what is furthermore important, they are present in various degrees of subdivision. Thus the softening point of the material as a whole is not only influenced by the melting points of its individual constituents, but also by their variety and state of division. As pointed out above, it is a question of progressive fusion according to the laws of solution. Strictly speaking, the actual melting point of a single homogeneous mineral is only roughly determined by its collapse and loss of shape, for in many cases the degree of viscosity just below the true melting point is nearly the same as the rigidity of the crystal. The alkali-felspars form a notable example. The true melting point is indicated by a discontinuous change of state, that is, of physical properties; for example, the temperature at which latent heat is absorbed in melting, or the change from the anisotropic to the isotropic state. These matters are sometimes complicated by polymorphism, however. The melting points of all the common minerals have been determined, but in only a few cases can the results be taken as reliable, owing to the faulty methods employed. In connection with refractory materials the following examples may be cited; there is no doubt about the accuracy of the first three:

Quartz; 1600° C.; inverts to tridymite at 800° (Day and Shepherd).

Albite-felspar; about 1230° C. (Day and Allen). Orthoclase-felspar, probably about the same.

Fluorspar; 1387° C. (Day).

Hæmatite; 1300° C. (Brun).

Magnetite; 1260° C. (Brun).

With regard to the influence of pressure on melting points of rock-forming minerals, it seems most probable that with increase of pressure the melting point also rises until a maximum is reached, and then with further increase falls again.

*Permeability.*—In certain metallurgical operations the degree of permeability of a fire-brick assumes a position of great importance, in so far as the capacity of the brick to resist the penetration of molten slags and volatilised substances is concerned. In this respect it is usual to determine the porosity of the material, but as this by no means corresponds to susceptibility of penetration, it seems better to attach greater importance to what directly measures this property, namely the permeability. Previously cited examples have made it sufficiently clear that access to slags and gases must be prevented, as much as possible. So far as the former is concerned, a very good idea of the value of a brick from this particular point of view could be gained by the application of what might be called "Rigg's Penetration Test."[1] In this a certain sized cube of the usual type of slag with which the bricks are likely to be brought into contact is placed upon the upper surface of a sample, and both are raised to a certain temperature under conditions which most closely approach those actually holding within the furnace itself. Subsequently the type and degree of penetration are noted, and the affected portions of the brick examined under the microscope for additional evidence. The ratio of the volume occupied by the pore-spaces to the total volume of the test-piece, that is, the actual porosity, may be diminished by reducing the size and number of the grog-particles. As frequently pointed out, this has the unfortunate effect, however, of rendering the brick more liable to crack or disintegrate under sudden changes of temperature. Possibly the easiest way of overcoming this difficulty would be to effect a compromise in the texture of the material so as to obtain the minimum of porosity, coupled with a sufficient inertness to rapidly fluctuating temperatures. In addition to this, however, there would seem to be a more efficient way of obtaining similar, and probably much better, results, and that is, by reducing the permeability to a minimum, and at the same time keeping the porosity fairly high. This could be done, for instance, by decreasing the size of the pores and increasing their number, or by keeping the pores large, and cutting off all intercommunication by burning the bricks at a temperature high enough to partly sinter the bond-material, which would naturally take place from the walls of the pores outwards. With regard to the first of these, it is important to test on a large scale the suggestions made by Rigg[1] on the advisability of effecting close packing by angular and graded grog, in conjunction with the use of a minimum amount of bond.

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[1] *Journal of Industrial and Engineering Chemistry*, 1913, vol. v. pp. 549–554.

*Resistance to Temperature Changes.*—This important property appears so far to have escaped standardisation, by which prescribed tests can be carried out on samples, and the results referred to a definite unit. In this connection it is interesting to note that a series of preliminary trials were carried out by Windzus[2] with the object of opening up an inquiry into the relationship between the size and amounts of grog-particles, and the capacity of the brick to withstand sudden changes of temperature. The test-pieces were heated for a certain time at a uniform temperature, and then rapidly cooled by exposing them for a certain time to a jet of cold air. After the bricks had then cooled down to the ordinary temperature, they were examined for cracks and any signs of disintegration. These, as well as other, observations have tended to show that, within certain limits, the coarser the grog, and the smaller the amount of bond, the less susceptible will the brick be to sudden variations in temperature. At the same time, however, the porosity is increased, and the crushing-strength tends on the whole to be diminished. In carrying out tests like the above, it would of course be necessary in the first place to make sure that the test-pieces had attained a definite and specified temperature, and that in every case they were cooled under standardised and uniform conditions for a certain length of time. Subsequent determinations of the ratio between initial and final crushing-strengths would probably give a substantial measure of the extent of disintegration, and microsections would afford sufficient evidence of the way in which this had taken place, thus offering clues for devising means of correction. In varying the proportions of grog and bond, one of the limits referred to above would be the attainment of a point when the bond had been so diminished in quantity as to prevent an efficient binding of the grog-particles into a coherent mass.

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[1] *Metallurgical and Chemical Engineering*, 1910, vol. viii. pp. 523–525.

[2] *Ibid.*, 1912, vol. x. p. 662.

*Dilatation.*—It is very important to know the extent to which a brick changes in volume with corresponding changes of temperature, and in order to distinguish these temporary changes from the permanent volume changes, usually referred to as "Contraction and Expansion," it might be of considerable advantage to make use of the term "dilatation." For instance the "Contraction and Expansion Test" in the gas engineers' specification refers to the linear elongation or contraction measured at normal temperatures, and after the test-piece had been heated for a certain time under specified conditions. Such measurements give the more or less permanent changes of volume, including the "residual contraction" of Mellor, and for the sake of clearness and distinction these changes might be called the "Permanent Expansion and Contraction," not by any means using the word "permanent" in its absolute sense. In any case it is, as previously remarked, a matter of obvious importance, especially in certain cases, to know the extent to which a brick will expand or contract with changes of temperature, and the difficulty of obtaining such information consists in having to make linear or volume measurements at high temperatures. So far, there appears to be no well-known and standardised method of carrying out these measurements in the case of fire-bricks, unless the instrument referred to by Baron Coppée is an example.[1] If, however, the question of standardising tests for refractory materials is seriously taken up in the future, and extended to include all branches of industry, it would not be a difficult matter to devise some means of measuring this dilatation, even at high temperatures. Besides these changes in volume of the material as a whole, there is also the question of internal dilatation among the constituent minerals, which cause either internal strains or differential movements, or both. Unless the brick is sufficiently burned, so as to cause fusion between the bond and the grog, the planes of contact will be planes of weakness, and in certain cases actual rupture may take place at these points. In some bricks it is easily possible, for instance, to remove the particles of grog from the surrounding matrix. Apart from this differential movement between grog and bond, there is also the setting up of strains or actual movement between the mineral constituents themselves, especially if the coefficients of dilatation of the several minerals differ in any considerable degree from one another. Some idea of the extent to which this proceeds would be given by the ratio of the crushing-strengths, determined before and after heating, especially if the heating and cooling were repeated a certain number of times. Likewise the actual effects could be readily examined under the microscope, whereby it is easy to see the strained or fractured condition of the particles. In polarised light a strained mineral shows undulating extinction.

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[1] *Journal of the Iron and Steel Institute*, 1913, No. II., p. 57.

So far as is known the volume of rock-forming minerals increases on heating, but as regards quantitative data we are at present very much in the dark. This also applies to all thermal and physical properties of minerals, with the exception of optical properties. Probably the coefficient of dilatation, between 0° and 100° C., ranges from 0·000016 in the case of orthoclase-felspar, to 0·000035 for quartz, the latter value approaching very closely that of iron. For the interval 0° to 1000° C. these mean values are nearly doubled. In minerals the coefficient of linear expansion is a vector quantity, and thus varies in different directions. Therefore when a brick cools, the shape, as well as the volume, of the constituents changes, and consequently complex systems of strains and stresses are set up. These may be relieved either by the opening of cleavage-cracks, or by movement of one mineral relative to another. On fusion the constituents expand, and if allowed to crystallise again they contract, so that if embedded in a glass, strains would be set up. Here again there are no direct experimental data of a quantitative kind, but the change at atmospheric temperatures can be calculated on knowing the specific gravities of crystal and glass. This change is apparently nearly the same at the melting point as it is at normal temperatures. In the case of quartz the value is 0·0734; in other words, the percentage expansion on passing from crystal to glass is 16·35. For anorthite-felspar it is 2·35 per cent. As regards aggregates of minerals it has been found that igneous rocks expand on fusion under normal pressures. In the case of bricks this is not necessarily the case on account of the porosity, and the tendency of the unfused particles to be drawn closer together.

*Permanent Expansion and Contraction.*—Details of the standardised test for determination of the linear change, before and after heating under prescribed conditions, are given in the gas engineers' specification. It will be noticed that the measurements are made at normal temperatures. Such measurements are valuable in giving an indication of the extent to which burning has been carried out, and the importance of eliminating "residual contraction" is of sufficient moment to justify repeated emphasis. Burning must be continued until internal fusion has taken place to such an extent that, firstly, the particles of grog and larger mineral constituents are sintered to the surrounding matrix, and secondly, until the pore-spaces are cut off from one another by impervious partitions, so as to reduce the permeability to a minimum. Comparative determinations of crushing-strength and examination of thin sections serve to control these factors.

*Hardness.*—In certain cases hardness becomes an important property in fire-bricks. Such will depend on the combined effect of several factors, such as mineral composition, density, and the extent of internal vitrification. Hardness is best determined by application of the standardised abrasion test for road materials, as used, for example, by the National Physical Laboratory, and the Department of Public Roads of the United States Government.[1]

*Toughness.*—The same applies to a determination of toughness, or capacity to resist impact, and can be conveniently measured by the attrition test as applied to road materials.

*Crushing-Strength.*—Instances have been recorded where useful information could be gained by measuring the crushing-strength, more particularly when made in conjunction with other tests. The determination is usually made by one of the hydraulic crushing machines after two opposing surfaces have been made perfectly even.

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[1] Richle Road Materials Testing Machine, Catalogue "K."

# APPARATUS FOR THE MEASUREMENT OF ELECTRIC RESISTANCE OF MATERIAL IN THE SOLID STATE AT HIGH TEMPERATURES,

## AND ITS APPLICATION TO THE DETERMINATION OF THE CRITICAL POINTS OF IRON AND STEEL.

By P. SALDAU (Professor at the School of Mines, Petrograd).

The thermal method, which is principally used for the determination of the transformations of metals in the solid state, cannot always be depended on to give satisfactory results, owing to its dependence upon the rate of cooling. In such cases the determination of the conductivity may prove a useful method, provided it is possible to find means to measure the electric resistance with accuracy.

Such a method would also provide an insight into the phenomena of transformations in the solid state, and help to clear up many points which the thermal method cannot always throw light upon. These considerations induced the author, at the suggestion of N. S. Kurnakoff, to study the question of the measurement of electric resistance at high temperatures. After having successfully used a provisional appliance of copper in the investigation of the gold-cadmium system[1] up to 700°, it only remained to substitute for copper a metal having a higher melting point and less oxidisable, in order to remedy the apparent defects in the appliance. The author was then able to proceed with the attempt to determine the critical points of iron and steel by the electric resistance method.

### I. Electric Resistance of Iron and Steels at High Temperatures.

The literature on the subject contains accounts of the investigations of Benoît,[2] F. Hopkinson,[3] H. Le Chatelier,[4] D. Morris,[5]

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[1] P. Saldau, *Imperial Russian Chemical Society*, vol. 46, 1914, p. 994 ; *International Journal of Metallography*, August 1914.

[2] *Comptes Rendus*, 1873, vol. 76, p. 342. [3] *Philosophical Transactions*, 1889, p. 443.

[4] *Comptes Rendus*, 1890, vol. 110, p. 283 ; 1890, vol. 111, p. 457.

[5] *Philosophical Magazine*, 1897, vol. 44, p. 247.

E. Harrison,[1] O. Boudouard,[2] and P. Fournel.[3] Since Boudouard refers to all the investigations preceding his own in his memoir published in the *Journal of the Iron and Steel Institute* in 1903, it is hardly necessary for the present author to do more than to mention briefly the work of P. Fournel. The results of his investigations are set forth in Table I.

TABLE I.

| No. | Composition. | | | Transformation Point. | | | Formulæ of the Straight Line Increase of the Electric Resistance at Temperatures above 900°. |
|---|---|---|---|---|---|---|---|
| | C. | Si. | Mn. | Ar3. | Ar2. | Ar1. | |
| I. | 0·08 | 0·24 | 0·43 | 880 | 775 | ... | $Rt = R900\ (1 + 3{\cdot}3 \times 10^{-4}t)$ |
| II. | 0·11 | 0·02 | 0·35 | 890 | 780 | 670 | $Rt = R900\ (1 + 3{\cdot}3 \times 10^{-4}t)$ |
| III. | 0·22 | 0·33 | 0·57 | 790 | 740 | 695 | $Rt = R900\ (1 + 4{\cdot}3 \times 10^{-4}t)$ |
| IV. | 0·37 | 0·126 | 0·47 | 730–770 | | | $Rt = R900\ (1 + 3{\cdot}8 \times 10^{-4}t)$ |
| V. | 1·05 | ? | 0·25 | 730–750 | | | $Rt = R900\ (1 + 4{\cdot}00 \times 10^{-4}t)$ |

Fournel concludes that the rise in the electric resistance at temperatures above 900° proceeds in accordance with the straight line formula $Rt = R900\ (1 + at)$, in which $a$ varies for the various steels. At temperatures under 600° the variation in the electric resistance falls into two divisions: from the ordinary room temperature up to a certain point the curve of the resistance variation follows a straight line, but beyond that point up to 600° it becomes parabolic. The boundary point between the rectilinear and the parabolic portion is lower the greater the impurity of the steel. Fournel explains this phenomenon as due to the formation of $\beta$-iron at the temperature corresponding to the boundary point. The same opinion is also held by F. Osmond,[4] who emphasises at the same time the importance of the results obtained by the measurement of the electric resistance.

*Apparatus.*—After a few unsuccessful attempts to produce an efficient vacuum at high temperatures, the author decided to carry out the heating in an inert gas, and for the sake of simplicity illuminating gas was used. The construction of the apparatus

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[1] *Philosophical Magazine*, 1902, vol. 3, p. 192.

[2] *Journal of the Iron and Steel Institute*, 1903, No. I. p. 299.

[3] *Comptes Rendus*, 1906, vol. 143, pp. 46, 287

[4] *Revue de Métallurgie*, 1906, p. 417.

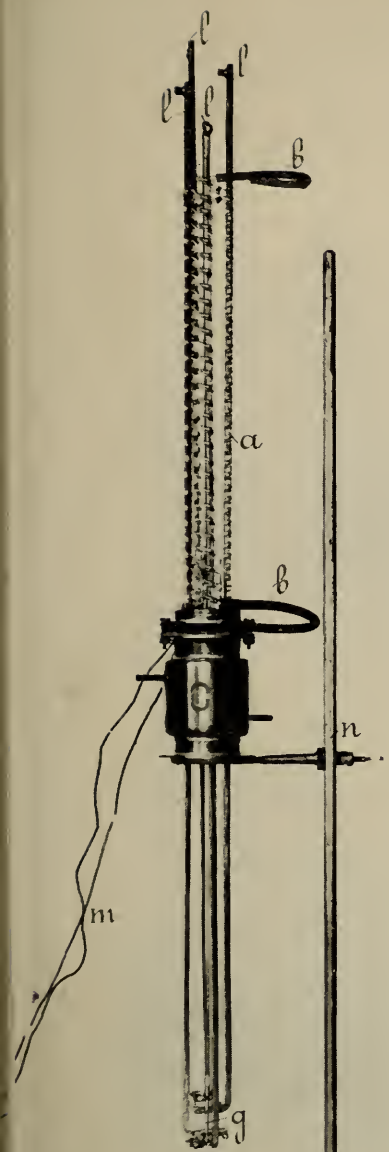

Fig. 2.

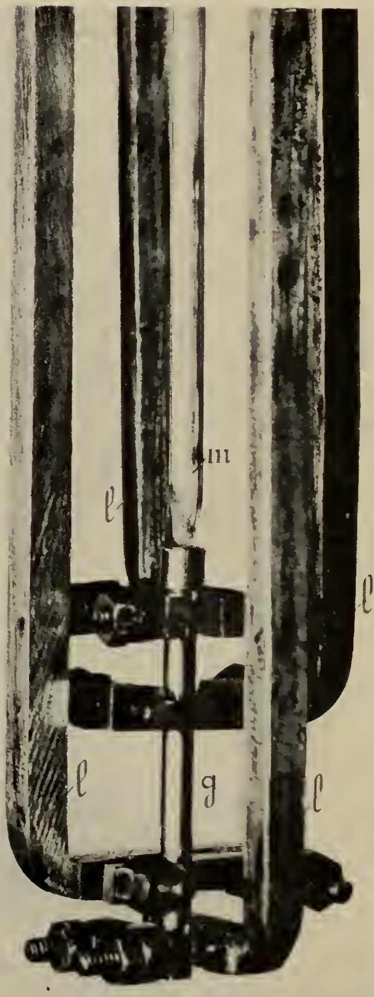

Fig. 3.

Arms conducting current ; *m*, Quartz insulation tube for the thermo element (Fig. 3) ; *m*, Thermo element (Fig. 2) ; *g*, Specimen under observation ; C, Coolers ; *a*, Glass coolers for supporting arms ; *b*, Rubber tubes for connecting the ends of the auxiliary coolers ; *n*, Support for use in changing the specimens to be examined.

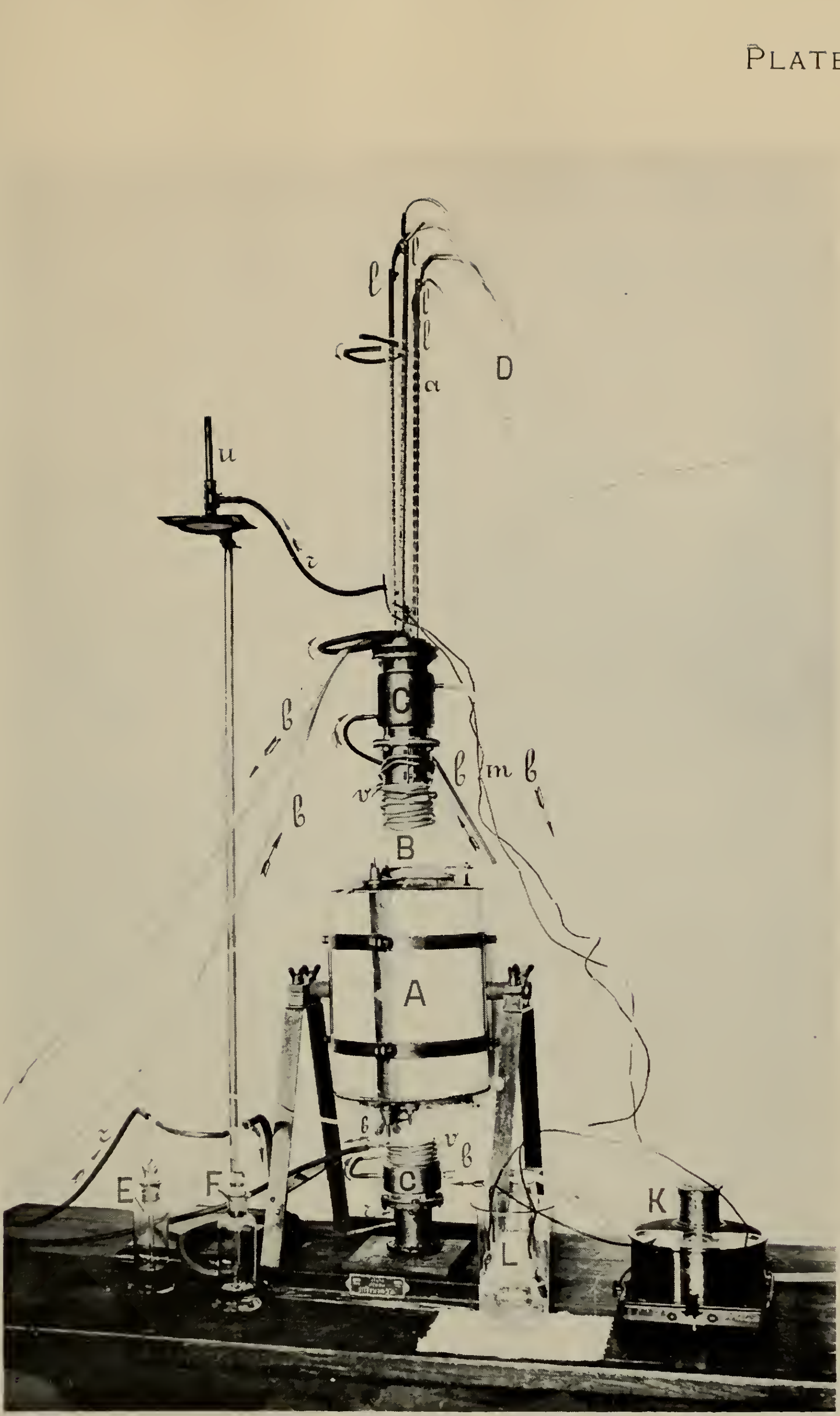

FIG. 4.

A, Electric furnace; B, Inner tube of hard porcelain; C, Coolers; D, Conductors to the Thompson double bridge; K, Galvanometer for measurement of temperature; L, Glass with ice water; E, Washing Flask, with alkaline pyrogallic acid; F, Washing Flask, with sulphuric acid; *a*, Auxiliary cooler for supporting arms; *b*, Rubber tubes for in-flow and out-flow of water; *l*, Supporting arms; *r*, Inlet and outlet tubes for gas; *u*, Gas burner; *v*, Lead cooling tubes.

was as follows : A Heraeus furnace (110 volts, 24 amperes), with an internal diameter of 65 millimetres, was used for heating, into which was inserted a hard porcelain tube of 50 millimetres diameter with two flanges. One flange was left in the condition as supplied by Heraeus, except that a cooler was fixed on to it. The second flange was replaced by a cooler with a vulcanite cover, through which the supporting rods were led. The supporting rods were coated with Mendelejeff's cement to a thickness of 1 centimetre. The arrangement of the cooler and the cover may be seen from Fig. 1.

The supporting rods of chrome nickel steel were inserted into tube B, and the alloys to be measured were laid on them. All dimensions were such that the apparatus could fit into a tube 50 millimetres diameter. The insulator tube of the thermo-element was so adjusted that its end was close up to the specimen. The arrangement of the supporting rods is shown in Figs. 2 and 3 (Plate XXIV.). The general arrangement of the whole apparat us during the experiment may be seen in Fig. 4 (Plate XXV.).

*Preparation of the Material.*—As material for the experiments, Kahlbaum and electrolytic iron and round forged iron and steel of 20 millimetres diameter were used. From these small bars of 5 millimetres diameter and 50 millimetres length were turned and polished. The bars were afterwards annealed for one hour at 1050° under a protective covering slag consisting of two-thirds $BaCl_2$ plus one-third KCl, and were slowly cooled down in thirteen hours. The composition of the material is shown in Table II. p. 221.

*The Experiments.*—The illuminating gas was first passed through a solution of pyrogallic acid in caustic soda to remove the free oxygen, and then through sulphuric acid to remove the moisture. On issuing from the apparatus the gas was burnt in an ordinary Bunsen burner. The purification as described proved sufficient, since neither the metal parts of the apparatus nor the specimens were oxidised in heating, and the constancy of the electric resistance (at $0{\cdot}12 - 0{\cdot}54$ microhm per cubic centimetre) before heating and after cooling was not affected. The resistance was measured twice by means of the Thompson double bridge, once during heating, and the second time during cooling. The heating from 680° to 1050° and the cooling through the same range were performed at the constant speed of 10° in five minutes. For

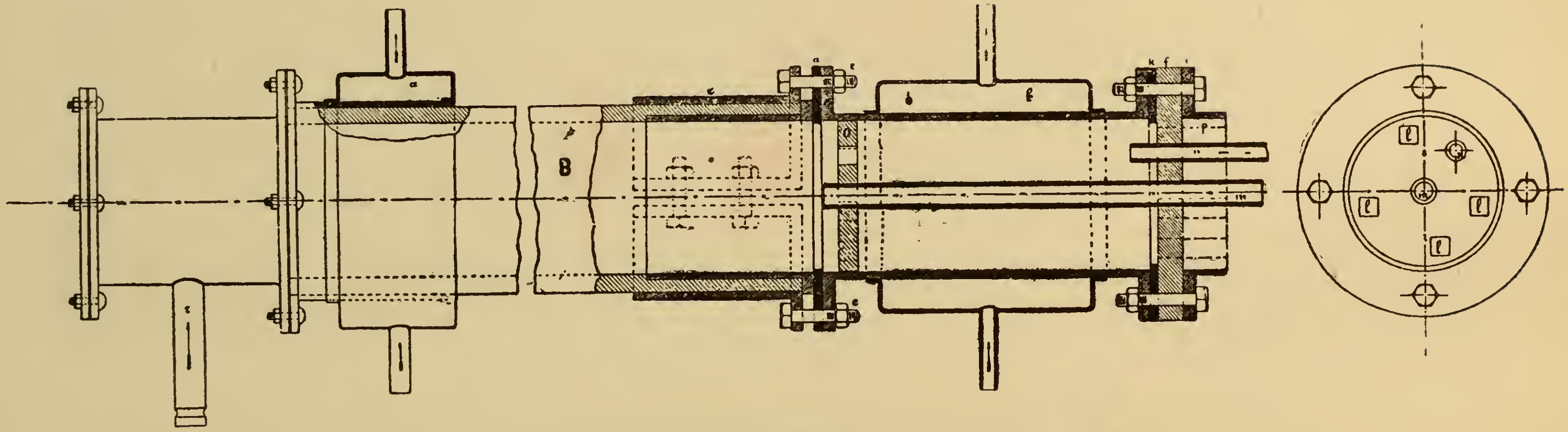
a
B
c
a
e
b
f
k
f
p
l
m

Fig. 1. Arrangement of Cooler and Cover.

the temperature measurements a Le Chatelier thermo-element was used with a Hartmann and Braun galvanometer calibrated according to the melting points of gold, silver, antimony, zinc, and tin.

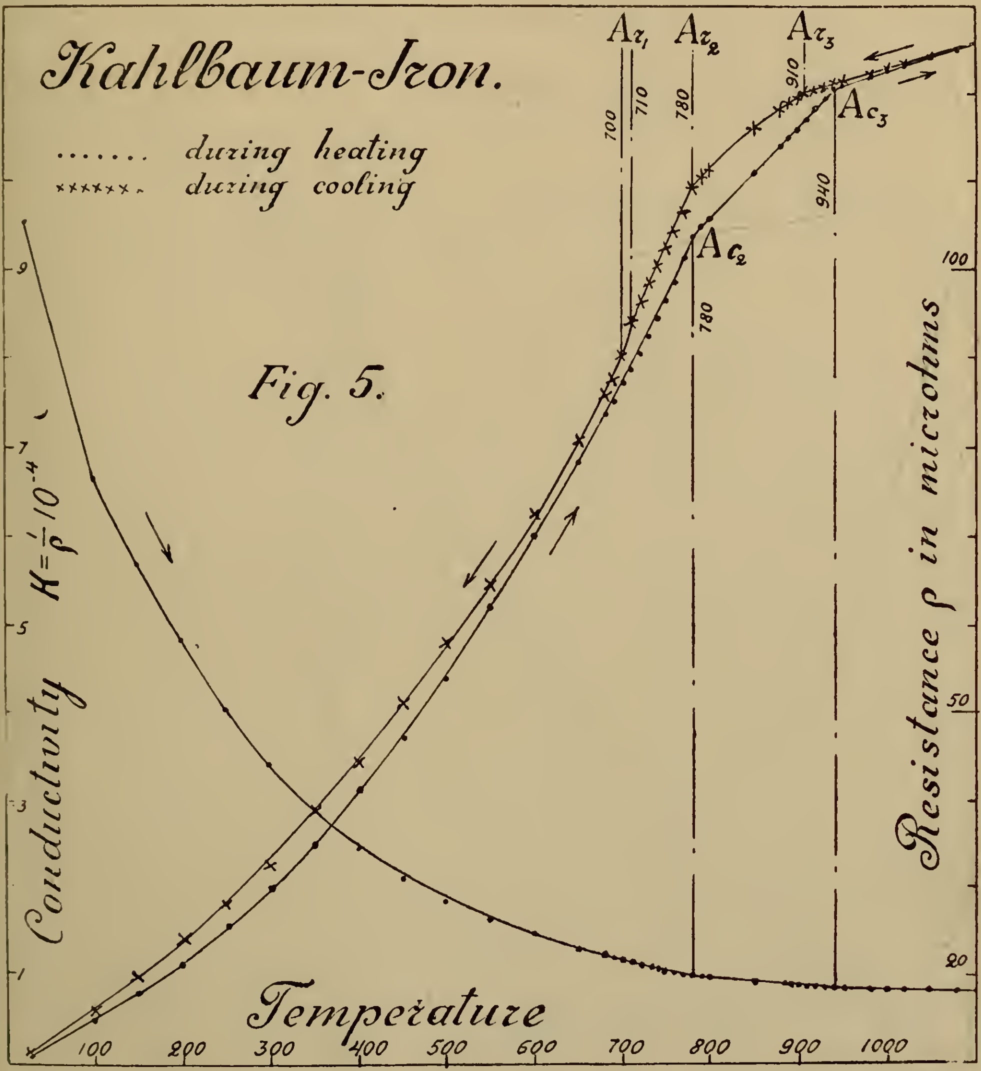

Fig. 5.

The results of the tests are summarised in Tables III. to IX., and are graphically represented in Figs. 5 to 18. It will be seen that the variation in the electric resistance describes a parabolic curve at temperatures up to 700°, the first portions of the curves up to 200° being considered as straight lines which are nearly identical for all the specimens. Attention is directed to the very remarkable fact that the electric resistance is not the same at one and the same temperature during heating and during cooling, but, as room temperature is approached, the difference between the resistance in heating and that in cooling tends towards zero. H. Le Chatelier[1] has already drawn attention to this phenomenon, and explains it as due to the difference in the speed of the transformations during heating and during cooling.

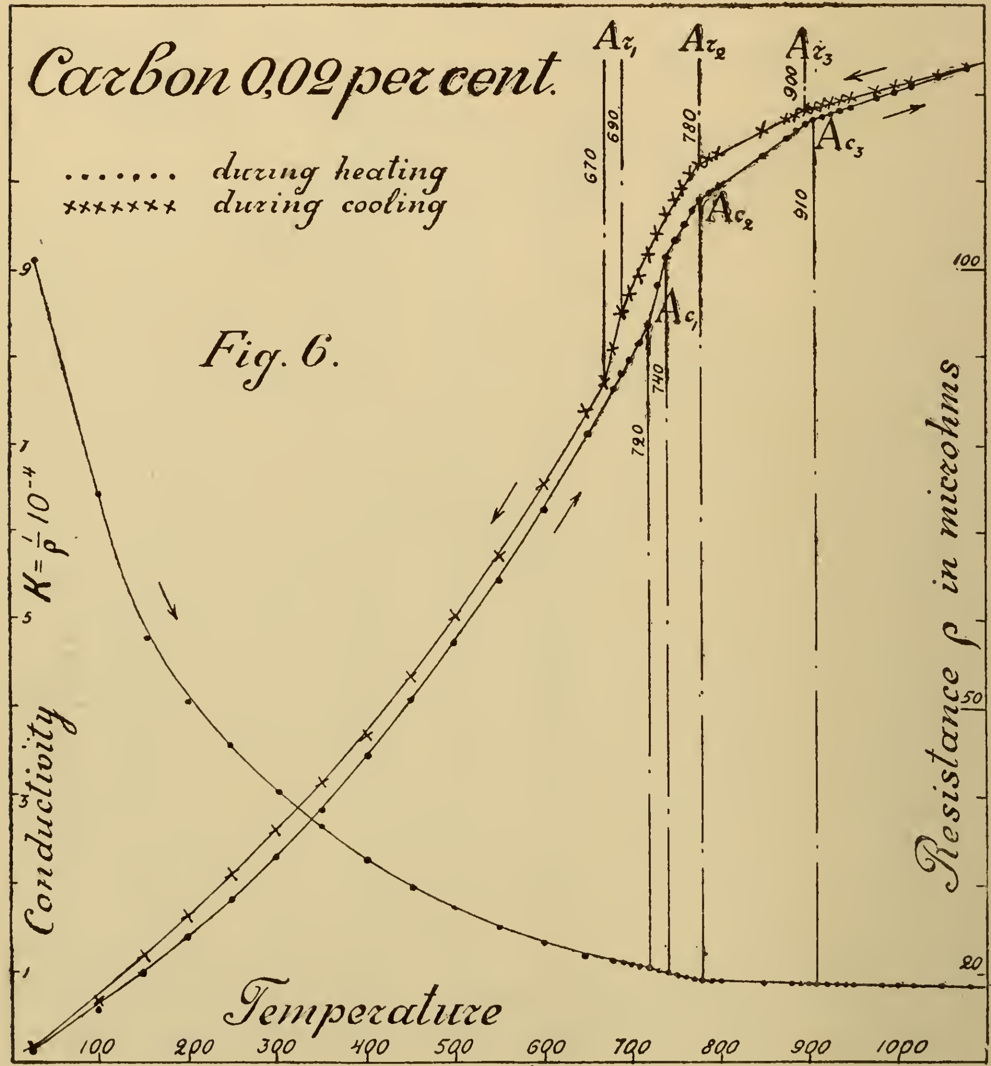

Fig. 6.

The diagrams, Figs. 5–18, show that the method of determining the critical points of iron and steel by measurement of the electric resistance gives sharply defined results, all these points being indicated by clearly marked breaks in the curve. The data from these diagrams are tabulated in Table X. and are shown plotted in Fig. 19, which gives the well-known diagram of the G.O.S.E lines of the iron-carbon system.

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[1] *Comptes Rendus*, 1890, p. 457.

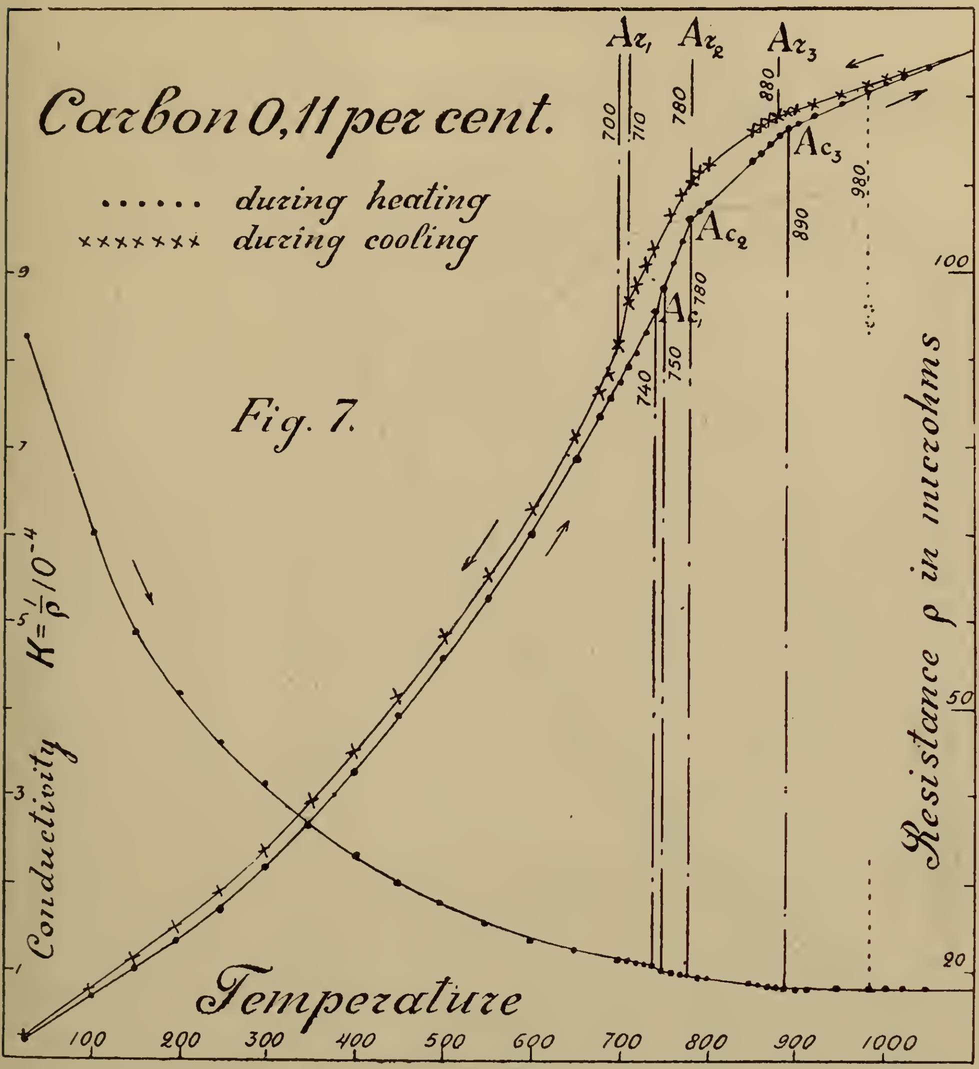

Fig. 7.

The investigation of the electric resistance at high temperatures has brought out some new features. Diagram, Fig. 5, shows that the Kahlbaum iron on heating has no Ac1 point, as is to be expected in the case of pure iron. The occurrence of Ar1 in cooling indicates therefore that during heating the iron has become slightly carburised, and confirmation of the carburisation is afforded by the fact that on cooling down to 25° the electric resistance has risen by 0·463 microhm per cubic centimetre. By comparison with the resistance of the electrolytic iron with 0·02 per cent. carbon, it would appear that a carburisation up to 0·01 per cent. carbon has taken place. This fact compels the conclusion that the Ar3 point of pure iron must be much higher than 910° as now generally accepted, and as indicated on diagram, Fig. 5.

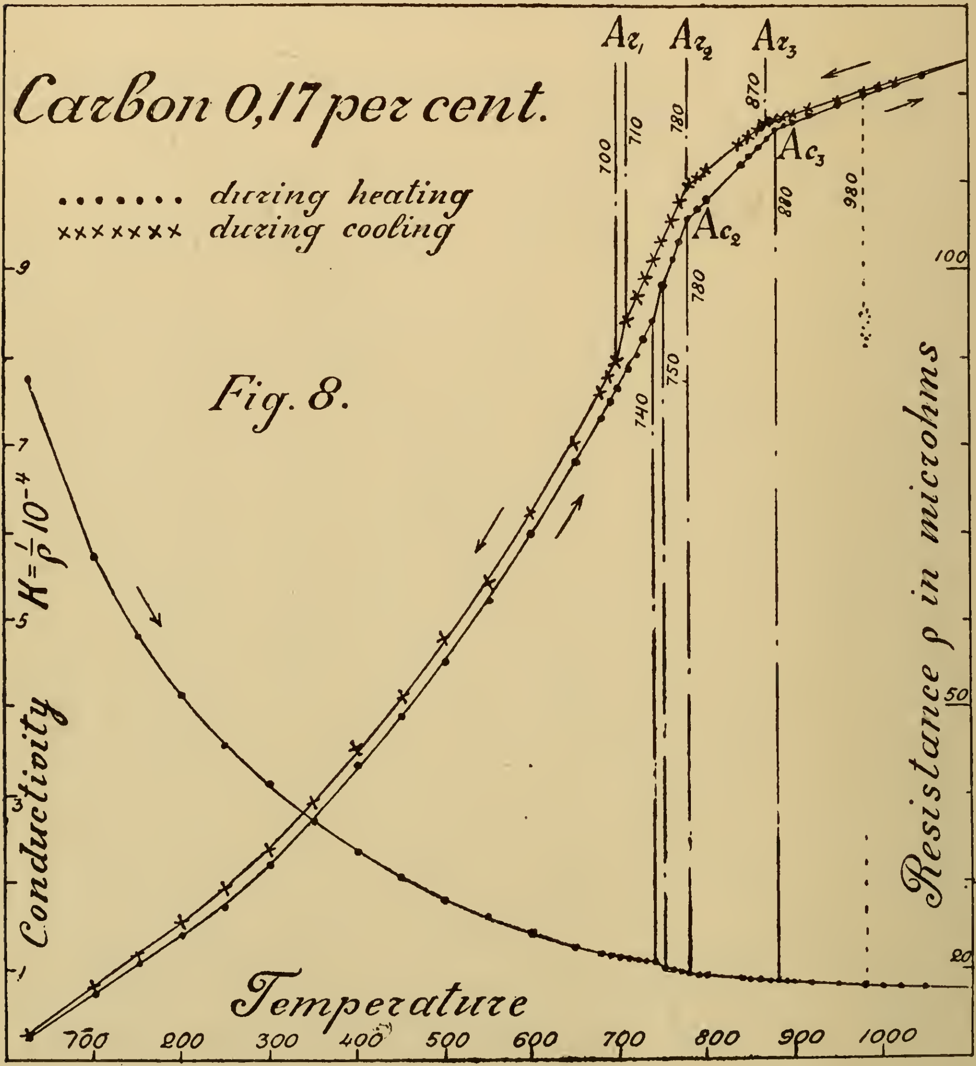

Fig. 8.

Thus, in the case of 0·02 per cent. carbon, there occurs on the transformation line G.O. a new break at 900°, as shown by the dotted line in Fig. 19. The author was, however, unable to determine how high the point Ar3 of pure iron actually lies, as he unfortunately had neither nitrogen nor a mercury vacuum pump at his disposal, but with these and the aid of the apparatus the question could no doubt be solved with great accuracy. Though very low-carbon iron becomes slightly carburised by illuminating gas, yet for steels of 0·35 to 1·5 per cent. carbon, the gas may be regarded as quite serviceable.

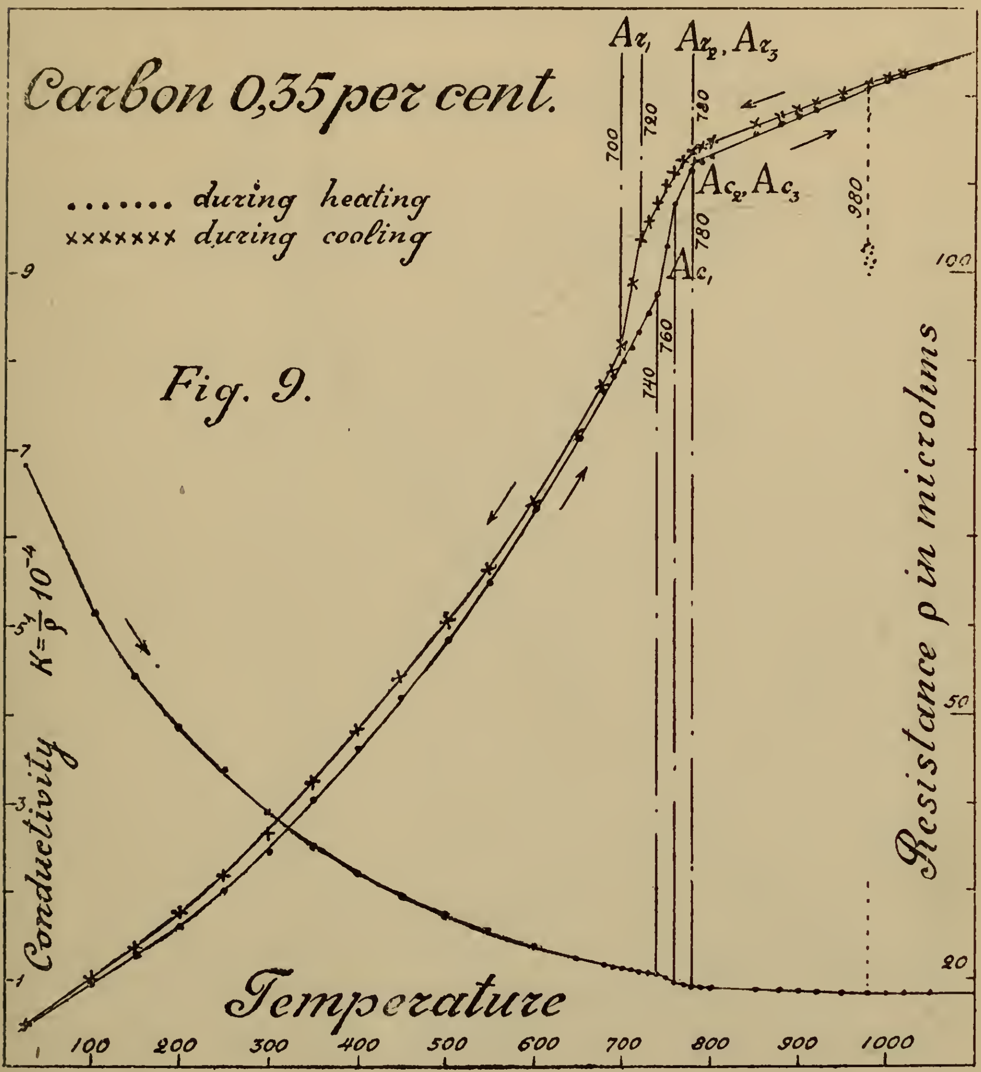

Fig. 9.

Another new feature is apparent from Figs. 7 to 15. The diagrams of the electric resistance of the 0·11 to 1·0 per cent. carbon steels show that the increase in the resistance at temperatures above 900° does not follow a straight line, as according to Fournel it should. All the curves show a break at

980°, indicating a new boundary line in the region of the $\gamma$ solid solution (austenite), which is represented on the diagram, Fig. 19, by the horizontal dotted line. Here the variation in the electric resistance occurs in heating and in cooling at one and the same

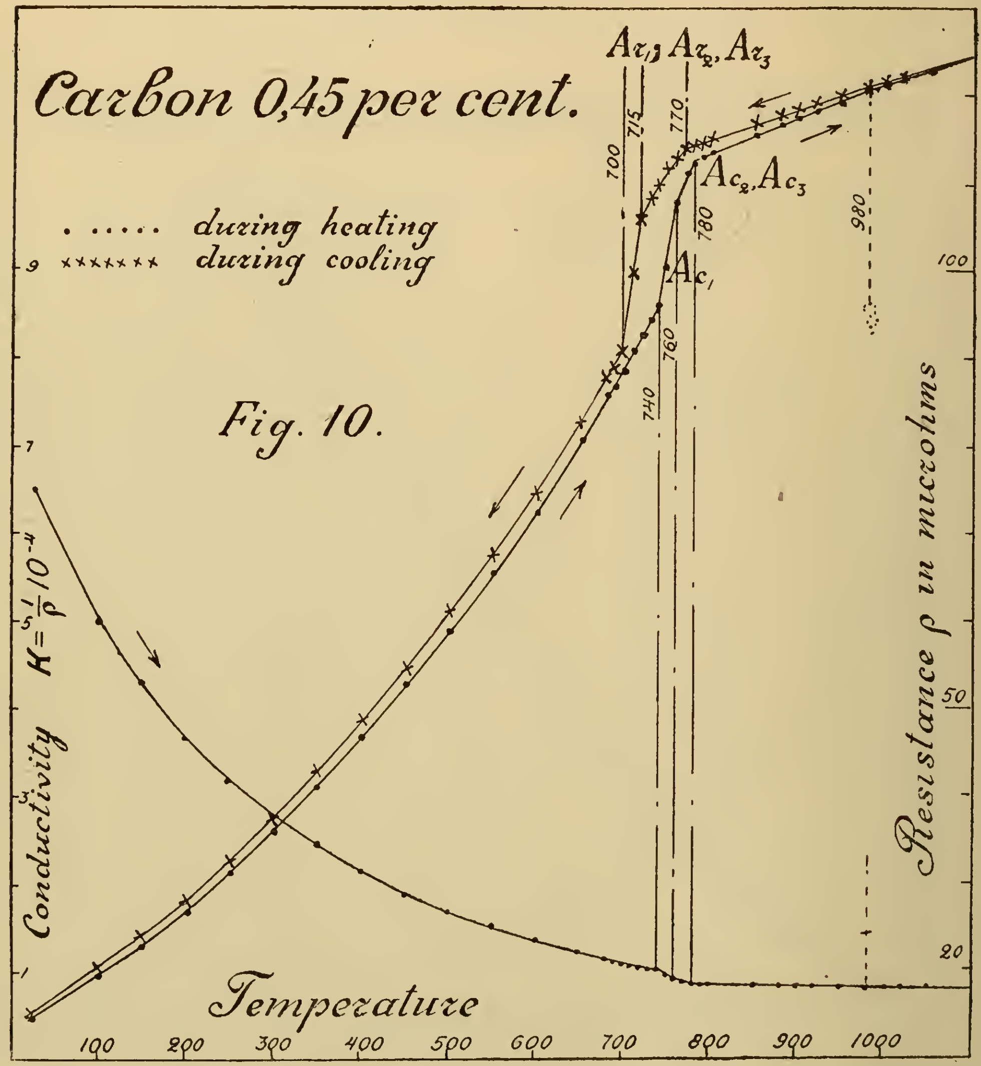

Fig. 10.

temperature. In this respect the new boundary line resembles the line of transformation of $\alpha$-iron into $\beta$-iron and *vice versa* at 780°. It cannot, however, be regarded as a line of transformation since the variation in the electric resistance is much too faintly indicated. A transformation, as is seen from the points A3, A2, A1, would be marked by a much stronger variation in the resistance. From the point of view of the "dispersoidal theory,"[1] the new phenomenon may well be explained by regarding it as the limit at which the growth of the crystallites of the *a* solid solution increases more rapidly than the temperature. The dispersoidal capacity is lowered by the crystallite growth, whereby the conductivity of the material is increased, that is, the resistance diminishes, which is exactly what happens at this point. From Ac3 to 980° the change of the temperature coefficient follows a straight line. That means that the crystallite growth proceeds in an even ratio with the temperature. But at 980° the temperature coefficient becomes slightly smaller, with a tendency

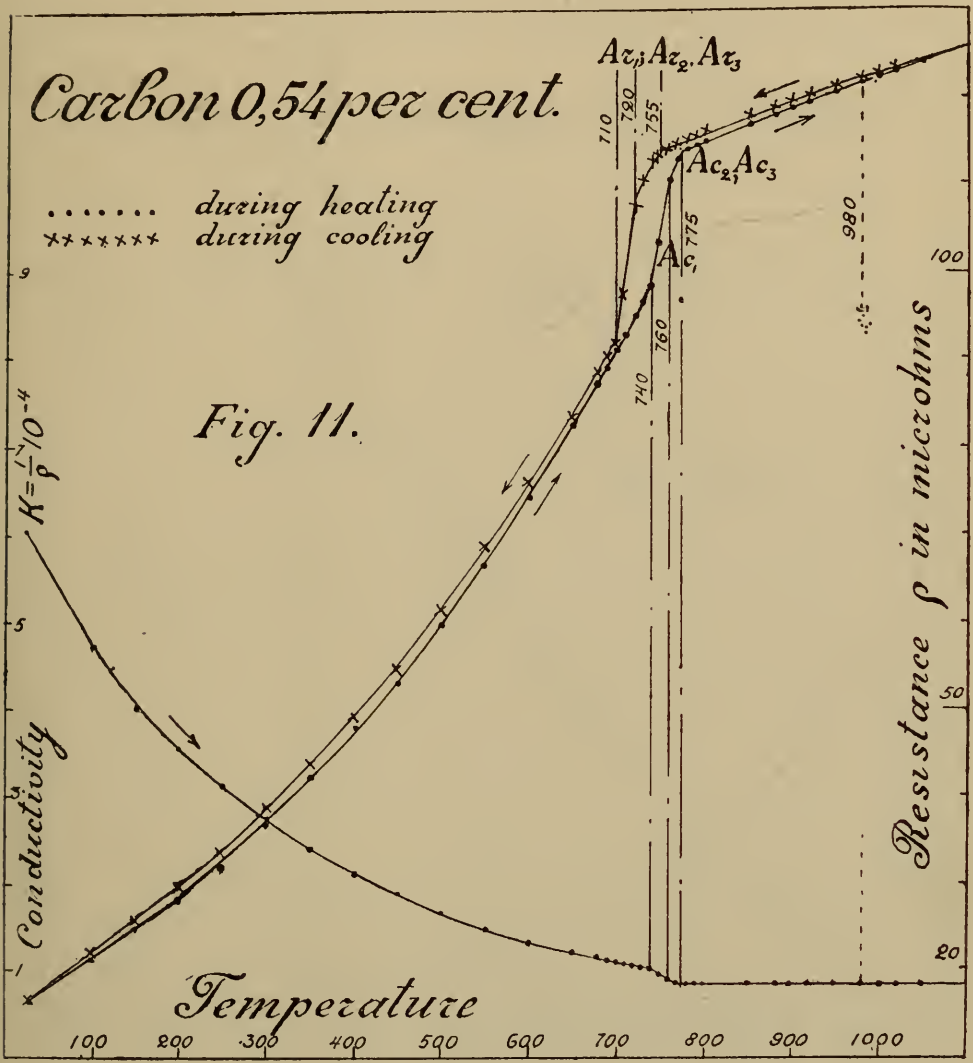

Fig. 11.

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[1] P. P. fan Weimarn, *International Journal of Metallography*, 1915, vol. 3, p. 65.

to decrease with an increase of temperature, an indication that the crystallite growth from 980° onward proceeds more rapidly than the rise in temperature. That is to say, the new boundary line at 980° indicates that from here onward the ratio of the rate of crystallite growth of the $\gamma$ solid solution (austenite) and of the rise of temperature is disturbed. The existence of such a boundary line between 880° and 950° in medium hard steels has already been pointed out by A. L. Boboschin[1] in 1911.

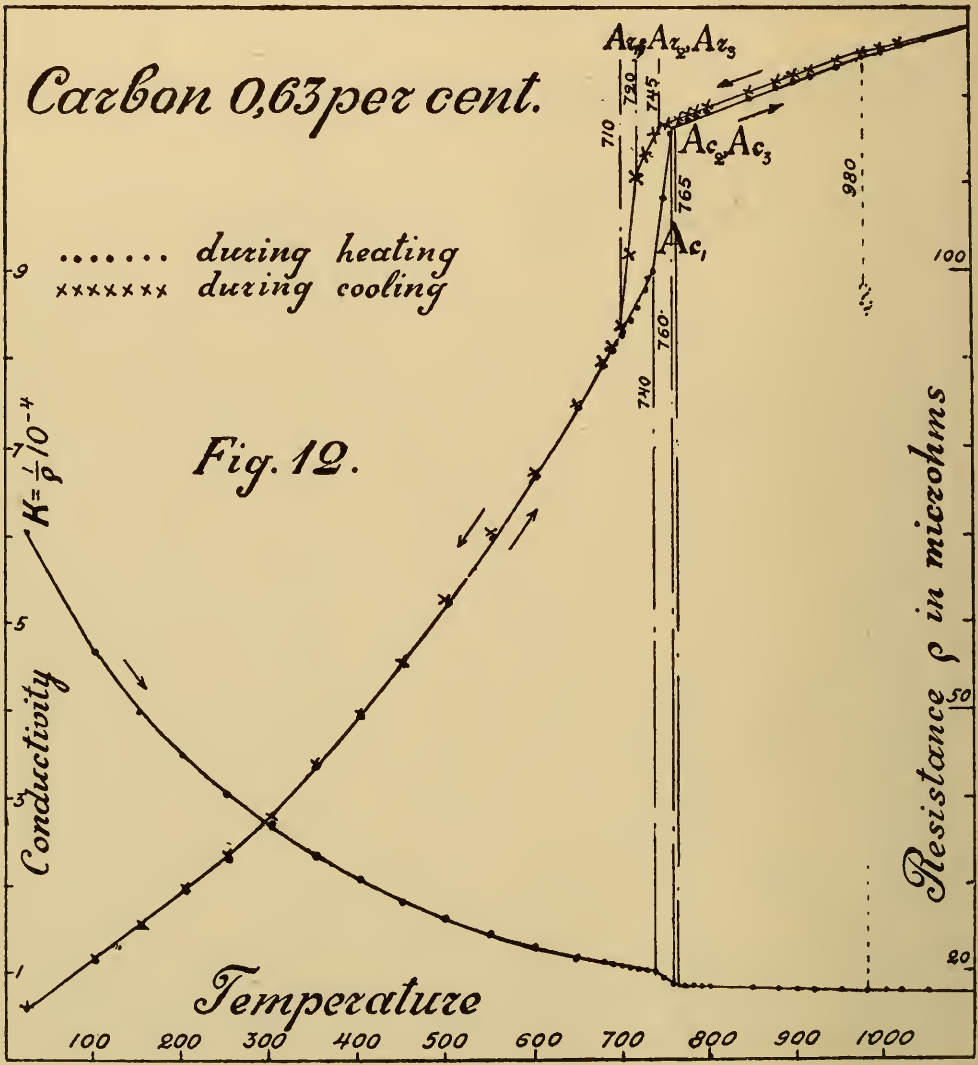

Fig. 12.

That this boundary has not been detected by means of the thermal method may be explained by the fact that probably no thermal effect takes place here. It is apparent from Fig. 19 that the transformation of $\gamma$ into $\beta$-iron is represented by a curve G.O., but the transformation lines of $\gamma$ into $\alpha$-iron and the solubility line of the iron carbide into $\gamma$-iron can be represented by straight lines O.S. and S.E.

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[1] *Journal of the Russian Society of Metallurgists*, 1911, p. 97.

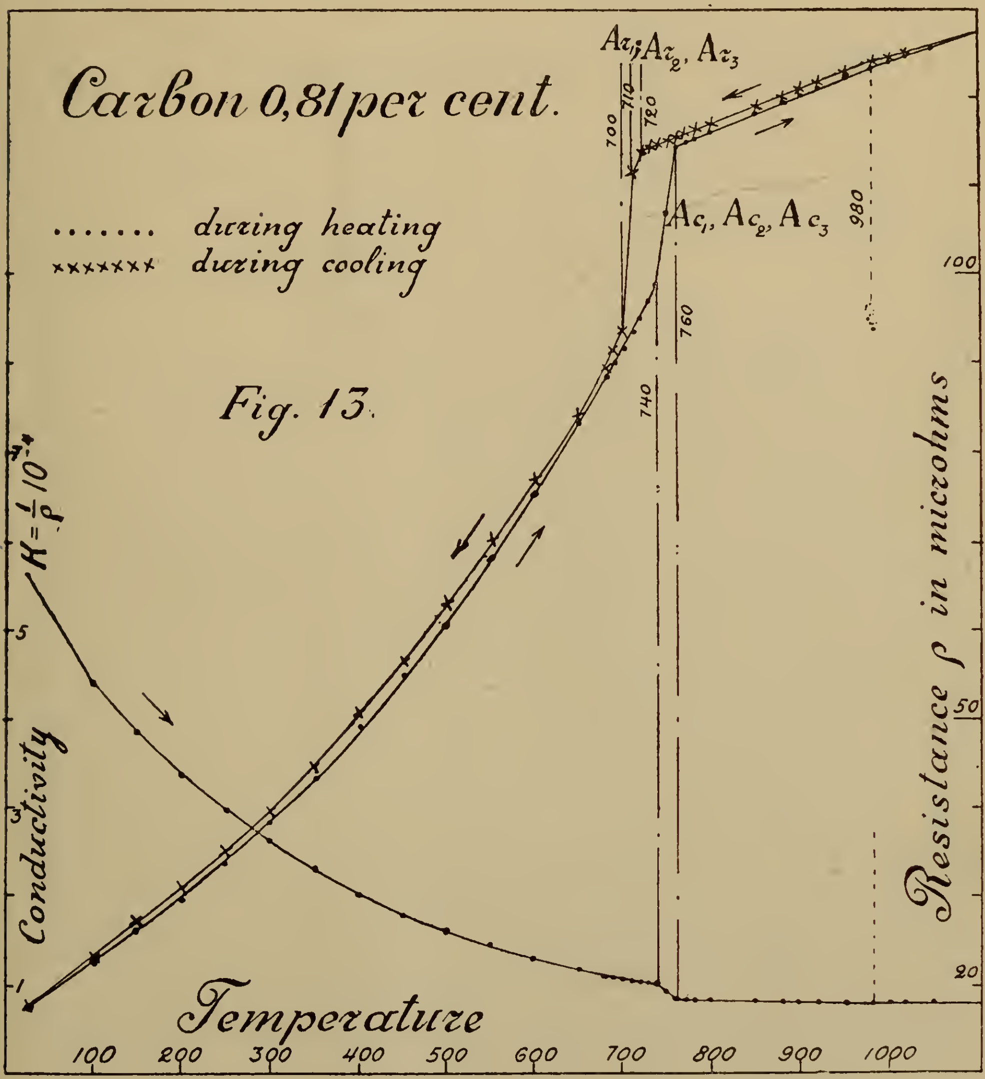

Fig. 13.

The change of $\alpha$-iron into $\beta$-iron and *vice versa* takes place at 780°.

The eutectoid line at a mean temperature of 707° extends to a carbon content of 0·02 to 0·01 per cent.

## II. INFLUENCE OF THE DISSOLVED CARBON ON THE ELECTRIC RESISTANCE OF IRON AND STEEL.

In 1904 C. Benedicks[1] evolved the following simple formula for the dependence of the electric resistance on the amount of carbon in solution in iron :

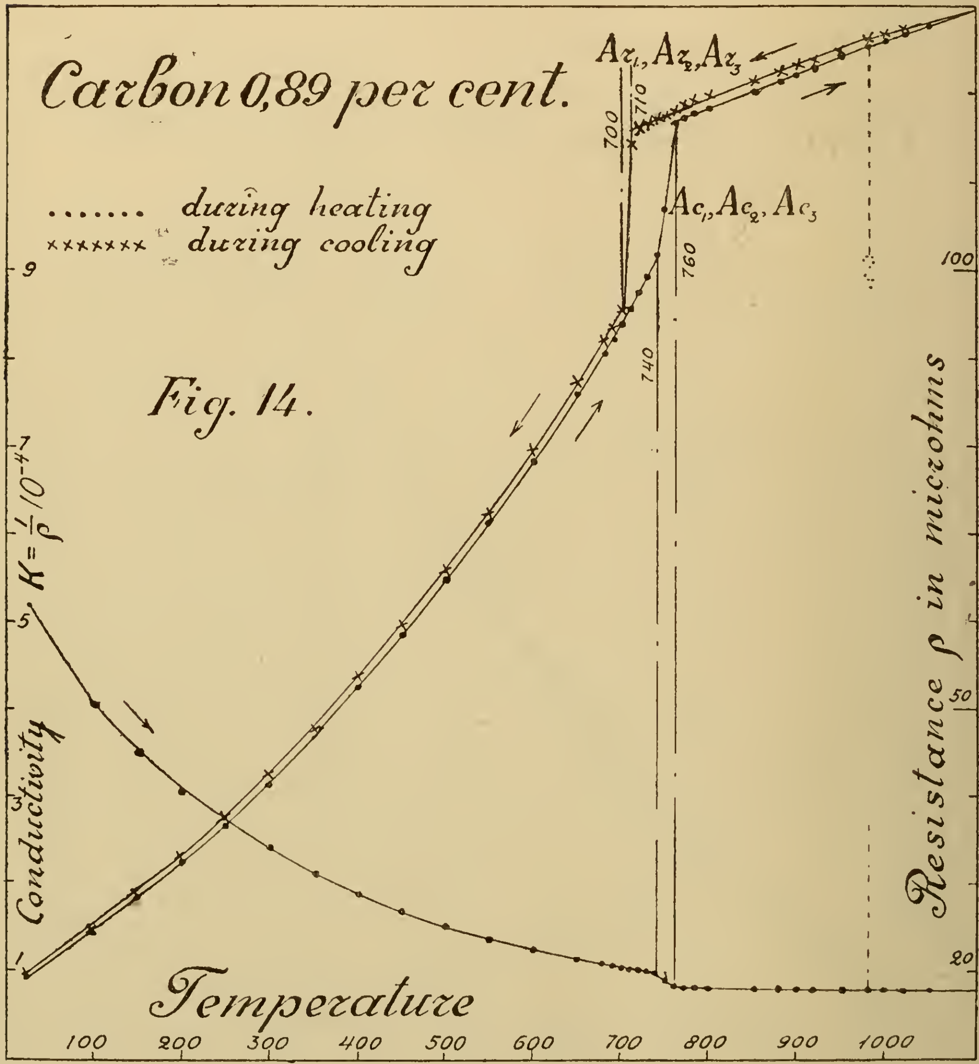

Fig. 14.

$\rho = 7{\cdot}6 + 26{\cdot}8\ \Sigma C$ microhms per cm.³, in which $\Sigma C = C + \frac{12{\cdot}00}{28{\cdot}4}\ Si + \frac{12{\cdot}00}{55{\cdot}00}\ Mn$, &c., and C, Si, Mn represent the constituents dissolved in the iron, according to the composition.

The experimental investigation of the electric resistance of the solid solutions of various systems has, however, shown that the variation in the resistance of all homogeneous solid solutions can be represented by a curve and never by a straight line, which is characteristic of a heterogeneous mixture. It seemed therefore very desirable, on the basis of the experiments on the resistance

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[1] *Recherches physiques et physico-chimiques sur l'acier au carbone*, Upsala, 1904.

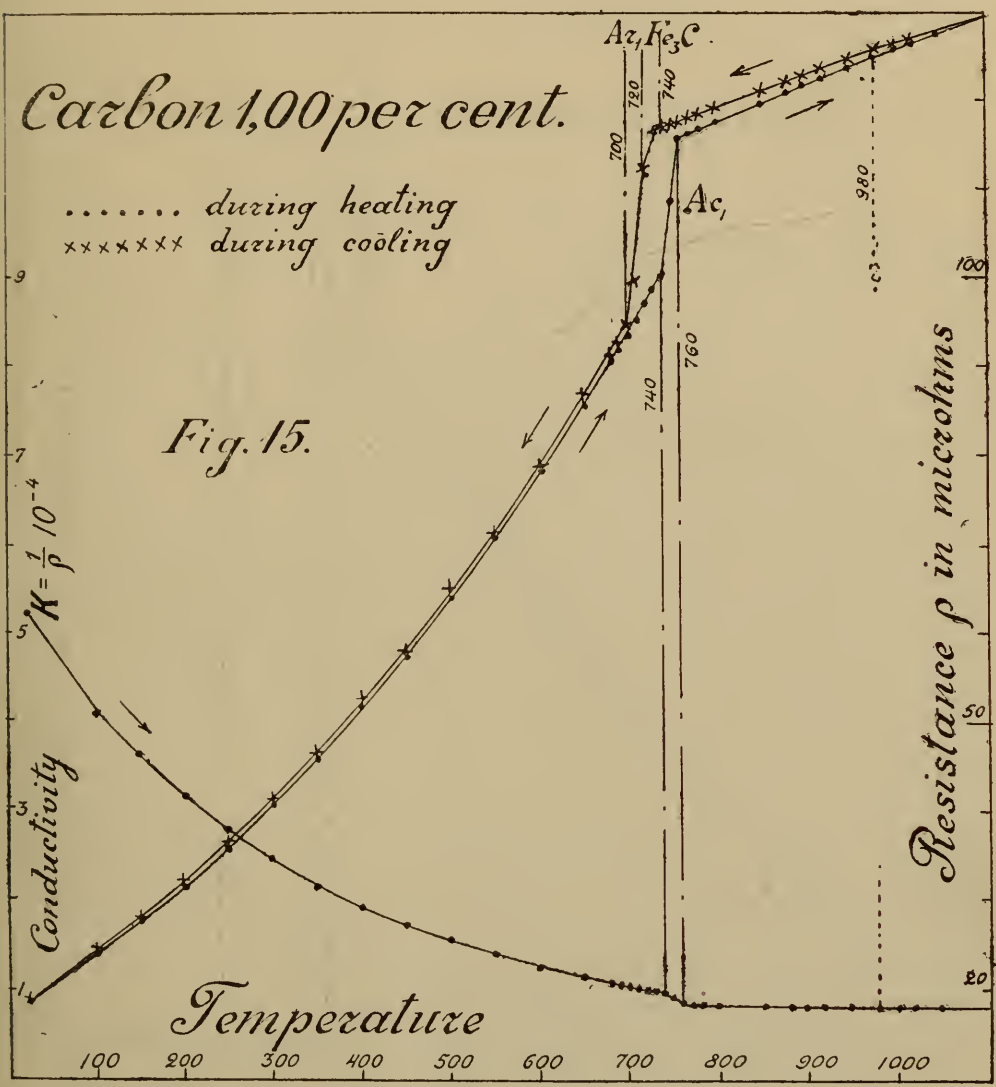


Fig. 15.

at high temperatures, to endeavour to account for the influence of the carbon in solution on the electric resistance. With this object, the isothermals of the resistance during heating and cooling deduced from Tables III. to IX. are shown in Figs. 20, 21, where it may be clearly seen that the isothermals do not follow a straight line, either above or below 900°.

Therefore the electric resistance of the $\gamma$ solid solution (austenite) varies according to a curve corresponding to the different amounts of carbon in solution, in the same way as has been observed in other homogeneous solid solutions.

The limits of the solid solution in the range above 760° in heating and up to 720° in cooling are indicated by the breaks in the isothermal curves.

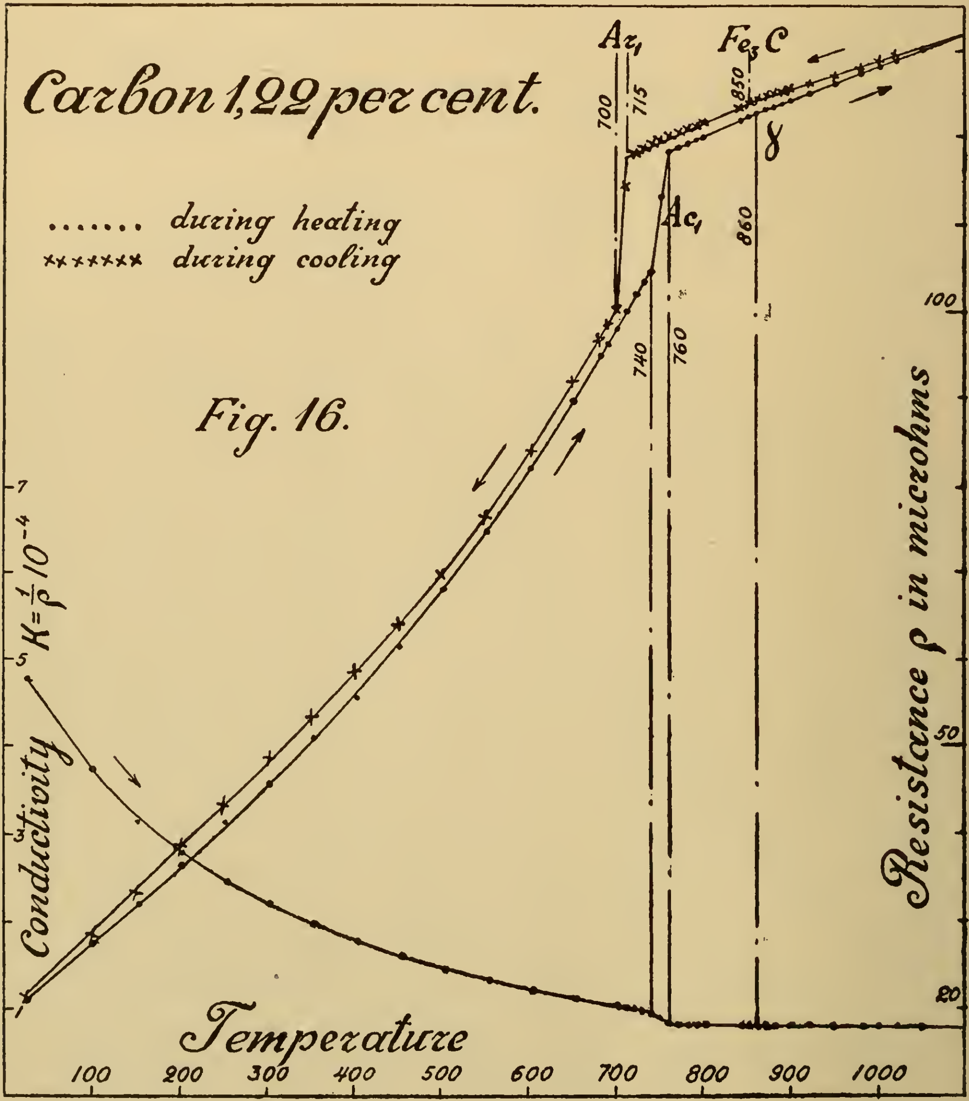


Fig. 16.

The isothermals above 900° show that the low carbon irons (0·01 to 0·11 per cent. carbon) have a higher electric resistance than the iron richer in carbon, a fact which is in contradiction to the usual supposition concerning the γ solid solution (austenite), according to which, at temperatures above 900°, the resistance of the low carbon iron ought to approximate to that of pure iron.

The increase in the resistance instead of a fall which one might expect, appears to confirm the fact mentioned in Section I. that the transformation line G.O. shows a break at 900°, and points to the conclusion that a new form of iron occurs at this point.

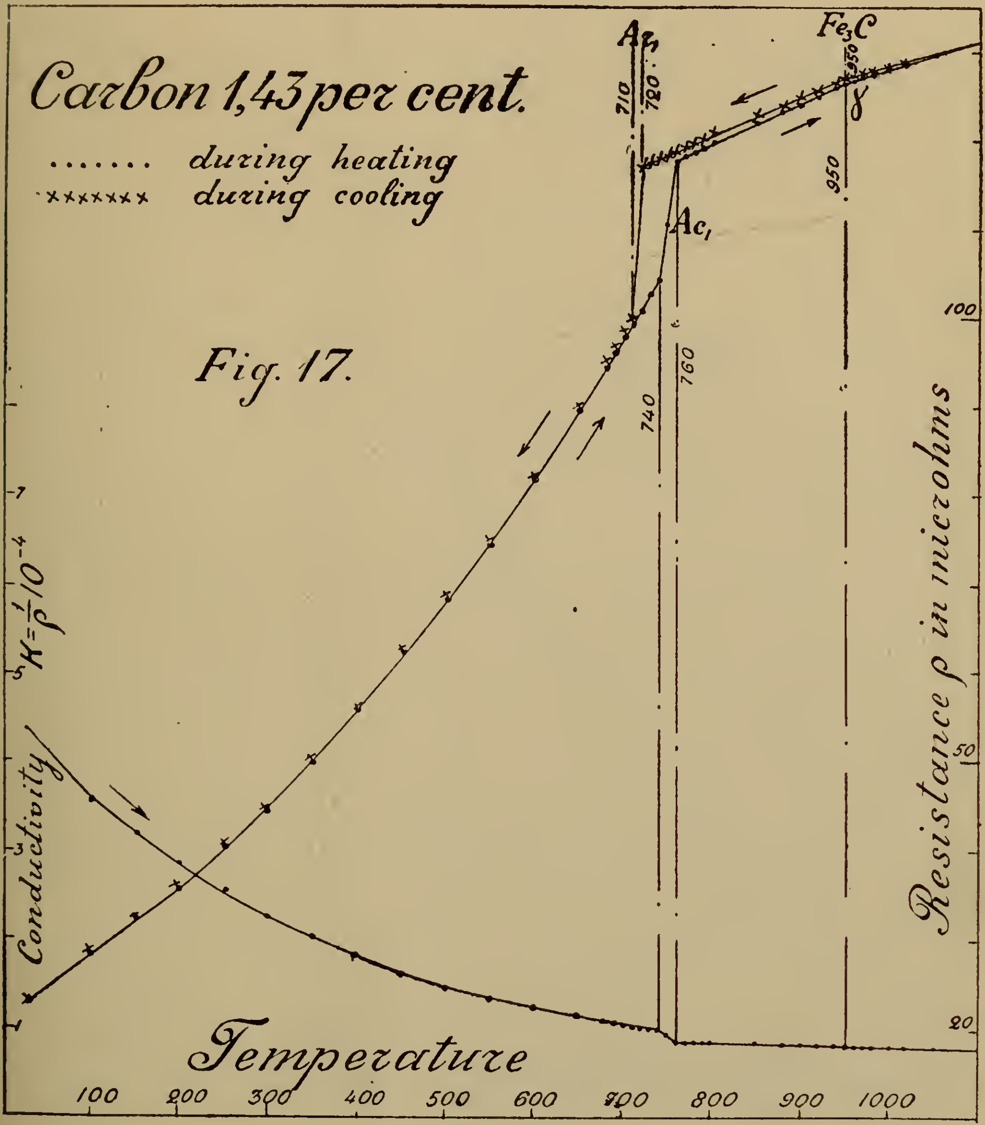
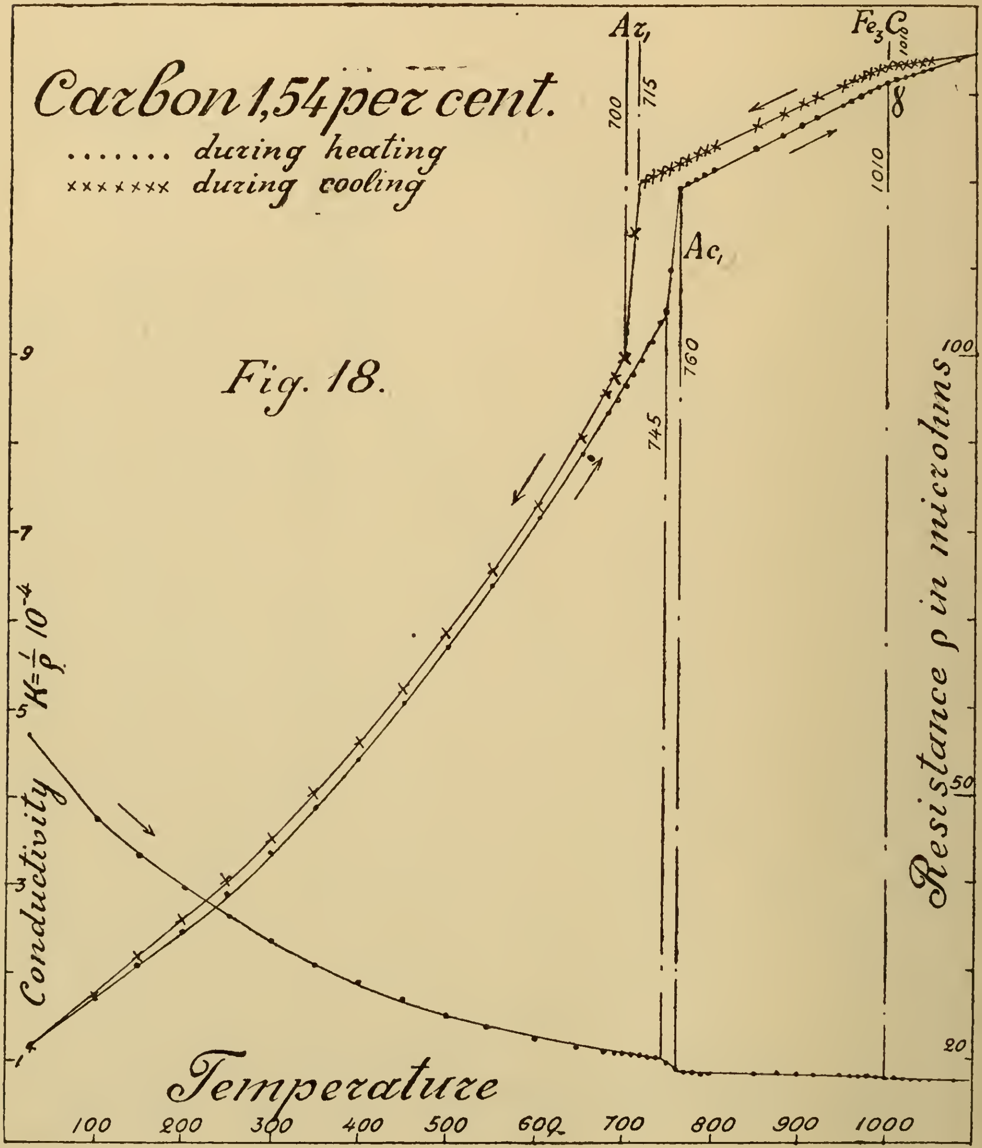
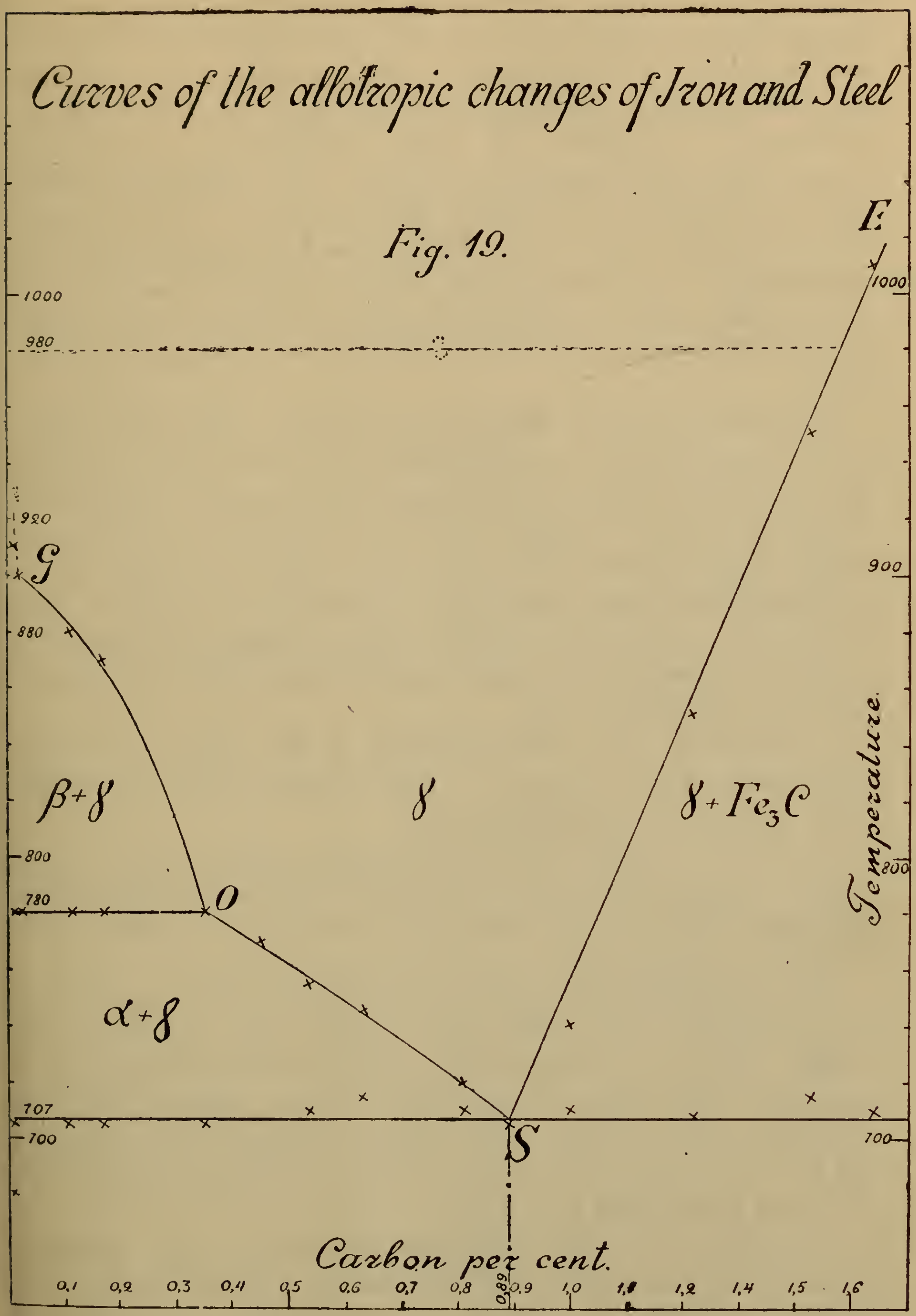


Fig. 17.

Other conclusions may also be drawn from the isothermals of the electric resistance. It will be noted that the eutectoid steel has a considerably higher resistance than the neighbouring steels, causing the isothermals to show at the corresponding point a relatively well-defined peak as a maximum. The fact that this maximum is very marked up to 760° in heating and from 720° in cooling, shows with great clearness that the physical properties of the steels depend not only on the composition but perhaps even more upon the dispersoidal degree of the material.



The isothermals at 760° in heating (Fig. 20) and 720° in cooling (Fig. 21) are of particular importance. At 760°, as Fig. 20 and



Curves of the allotropic changes of Iron and Steel

Fig. 19.

Figs. 5 to 18 show, the limit is reached from which, as the temperature continues to rise, the heterogeneous mixture of *α*-iron and iron carbide begins to change into the *γ* solid solution. At this moment, therefore, all stresses in the heterogeneous mixture are equalised and perfect equilibrium is established between the *α*-iron and the iron carbide. The physical properties of the heterogeneous mixture at 760°, and also in cooling at 720°, will then show up clearly. Figs. 20 and 21 indicate that the isothermals, from pure iron up to the eutectoid point, at 760° and at 720° rise in a continuous curve. At the eutectoid point the peak maximum occurs, after which the curve follows a straight line.

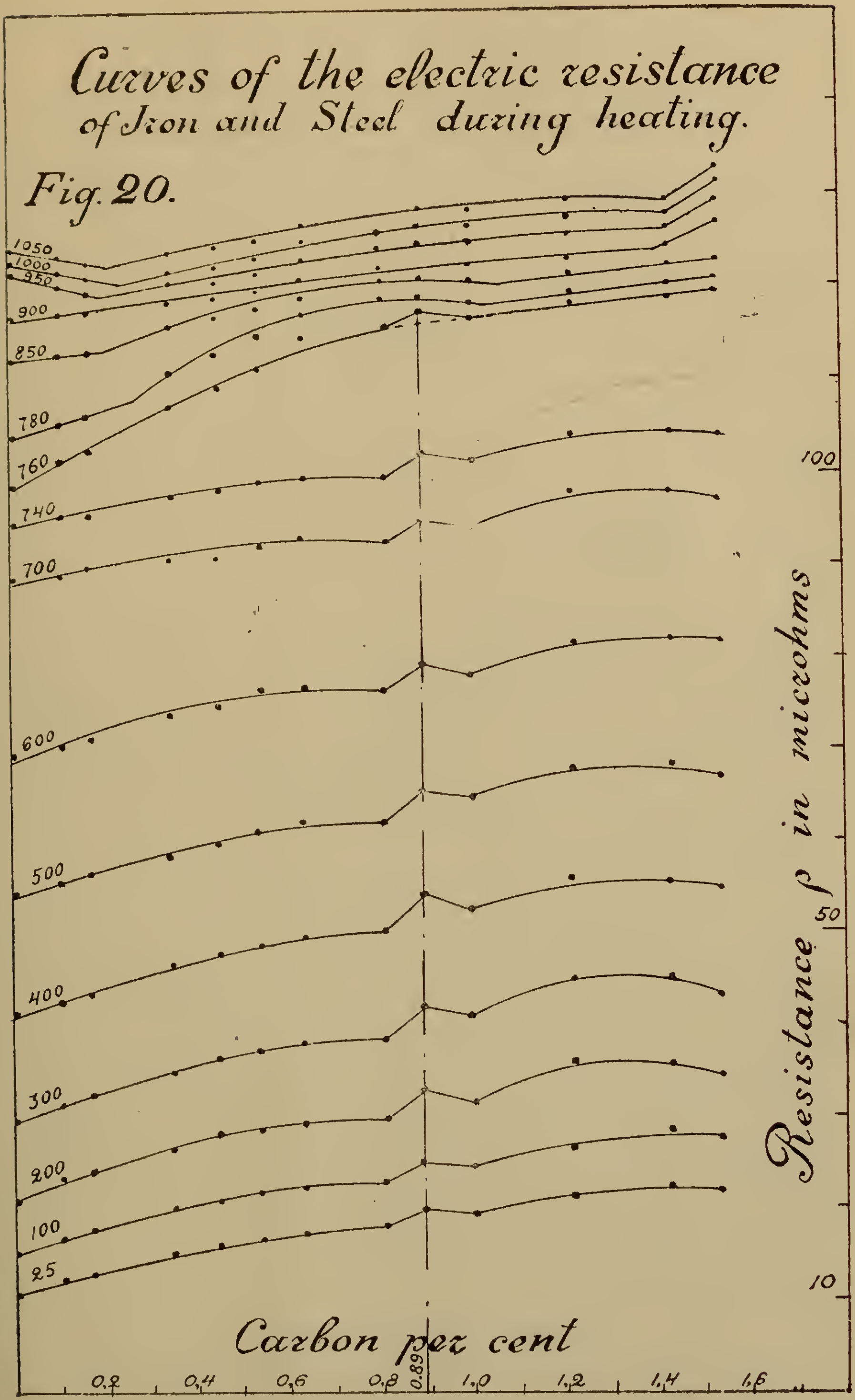
Neglecting the peak, caused by the higher dispersoidal degree of the eutectoid steel, a continuously rising curve and a tangent at the eutectoid point are obtained, as shown by the dotted lines. From this it may be judged that in the region of the continuous curve one of the two constituents, *α*-iron and iron carbide, of the heterogeneous mixture must have a variable composition. This leads to the conclusion that the *α*-iron absorbs a continuously increasing quantity of carbon, as the total carbon in the steel increases to 0·89 per cent.

C. Benedicks gives 0·27 per cent. as the maximum carbon dissolved in *α*-iron, but gives a total carbon content of 0·50 per cent. as the limit of the rising curve.

In order to compare the heated and the quenched state of the steel as regards the dissolved carbon, by means of the electric resistance method, three series of quenchings—from 950°, 900°, and 800°—were made.

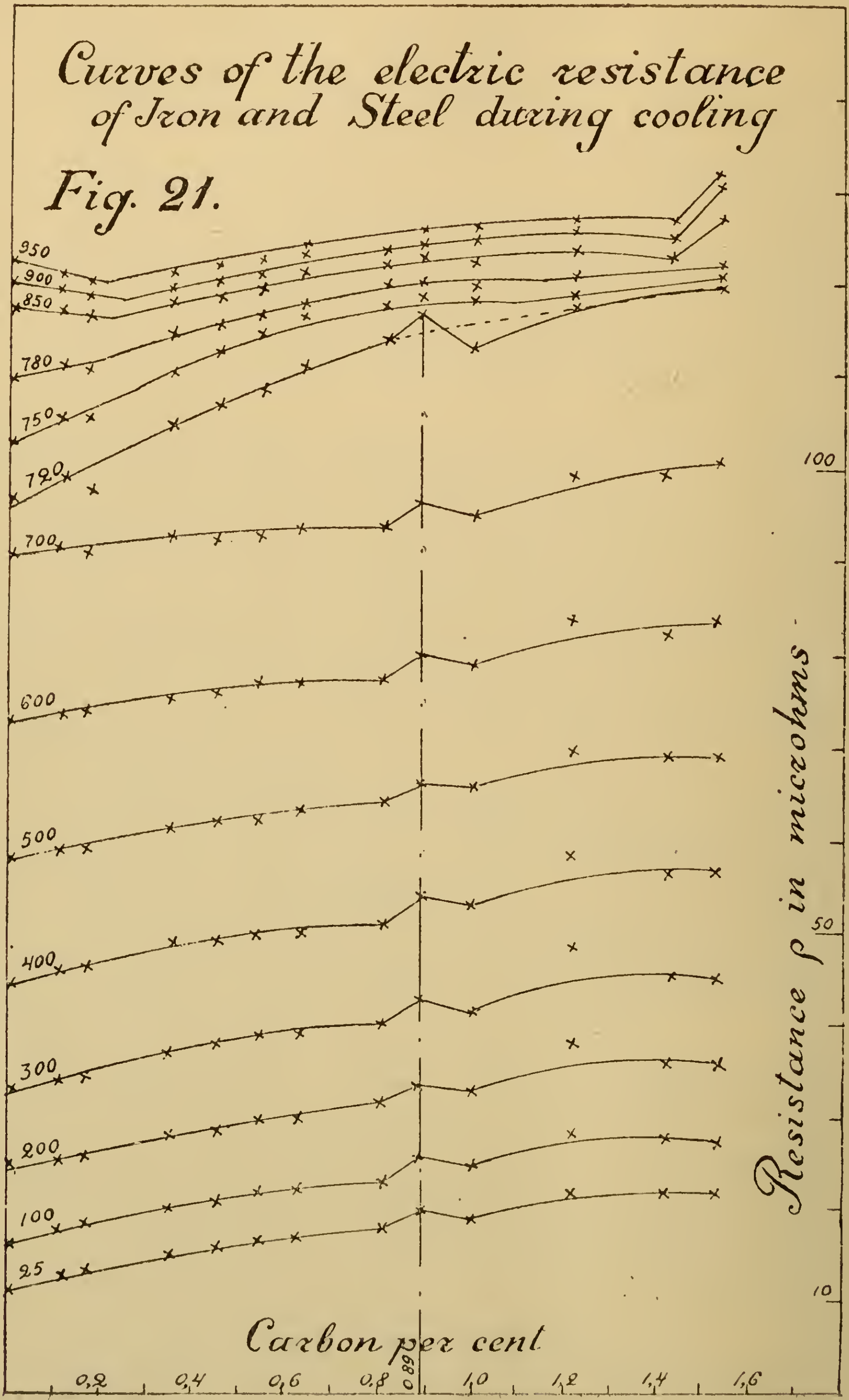
After measuring the electric resistance at high temperatures, the specimens were heated again under a slag covering up to 1050°. They were then slowly cooled to the quenching temperature, maintained at that point for ten minutes, and then quenched in ice water. The electric resistance was measured at 25° in the thermostat and the results are summarised in Table XI. and represented in Fig. 22.

From Fig. 22 it will be seen that for the steel in the quenched state, in the range of the dissolved carbon, the isothermals of the electric resistance do not follow a straight line. It is apparent from the isothermals that the eutectoid steel, even when quenched,



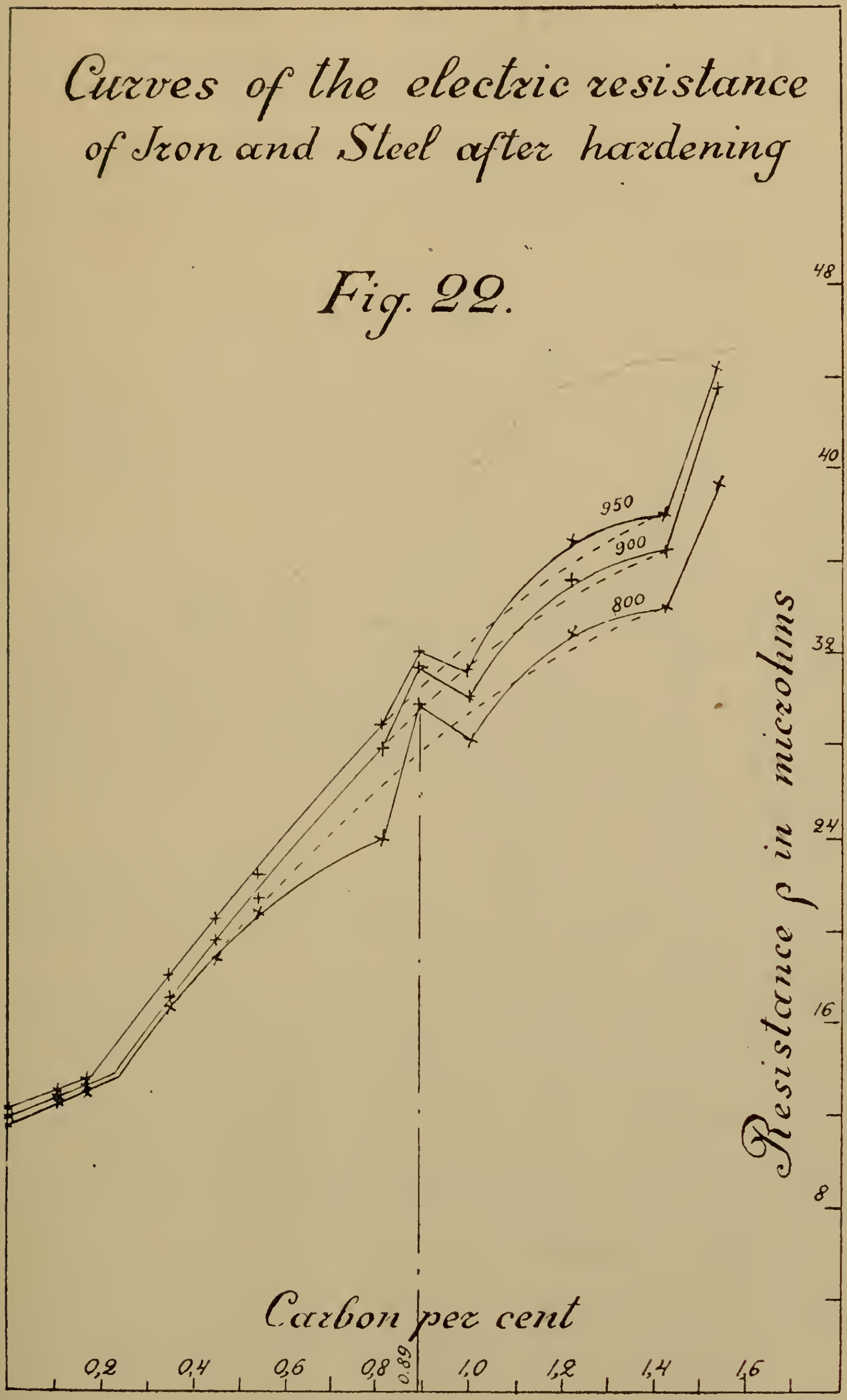
Curves of the electric resistance of Iron and Steel during heating.

Fig. 20.



Curves of the electric resistance of Iron and Steel during cooling

Fig. 21.



Curves of the electric resistance of Iron and Steel after hardening

Fig. 22.

undergoes a relative increase in the resistance, with the result that instead of obtaining a single curve following the course indicated by the dotted line, we have two curves between which lies the peak maximum of the eutectoid steel.

As regards the pure iron, the break in the isothermals of the resistance after quenching at 950° (Fig. 22) may again be regarded as evidence of the existence of the hypothetic new form of iron.

## SUMMARY.

1. An apparatus has been constructed for the measurement of the electric resistance in the solid state at high temperatures, which can be applied to the determination of the critical points of iron and steel.

2. With the aid of the measurement of the electric resistance at high temperatures, the diagram of the transformation line G.O.S. and the solubility line S.E. have been plotted. The lines of transformation of the $\gamma$ into $\beta$-iron can be represented by a curve G.O. with a new break at 900° and at a carbon content of 0·02 per cent., but the line of transformation of the $\gamma$ into $\alpha$-iron and the line of solubility of the iron carbide in $\gamma$ iron is represented by straight lines O.S. and S.E.

3. In the range of the $\gamma$ solid solution (austenite) a new boundary line has been found at 980°, thereby calling in question the correctness of Fournel's formula for the resistances at temperatures above 900°: $Rt = R900\ (1 + at)$.

4. It has also been shown that Benedicks' straight line formula of the resistance in relation to the carbon in solution in iron, $\rho = 7{\cdot}6 + 26{\cdot}8\ \Sigma C$, does not meet the conditions.

5. The eutectoid steel in the whole range of the heterogeneous mixture, up to 760° in heating and from 720° in cooling, has a relatively higher electric resistance than the steels on either side of the eutectoid composition.

## APPENDIX.

After recording the results of measurements taken from the specimens in the atmosphere of illuminating gas, the author was able to obtain some nitrogen, which enabled him to carry out a few supplementary observations on the specimens heated in nitrogen, in order to establish clearly the position of the critical point Ar3. The nitrogen was dried by filtering through sulphuric acid, red-hot copper, and phosphoric anhydride. The rate of heating and cooling was the same as in the case of the experiments with illuminating gas, and the results of the readings are given in Table V*a*. (p. 231) and are plotted in Figs. 5*a* and 5*b*.

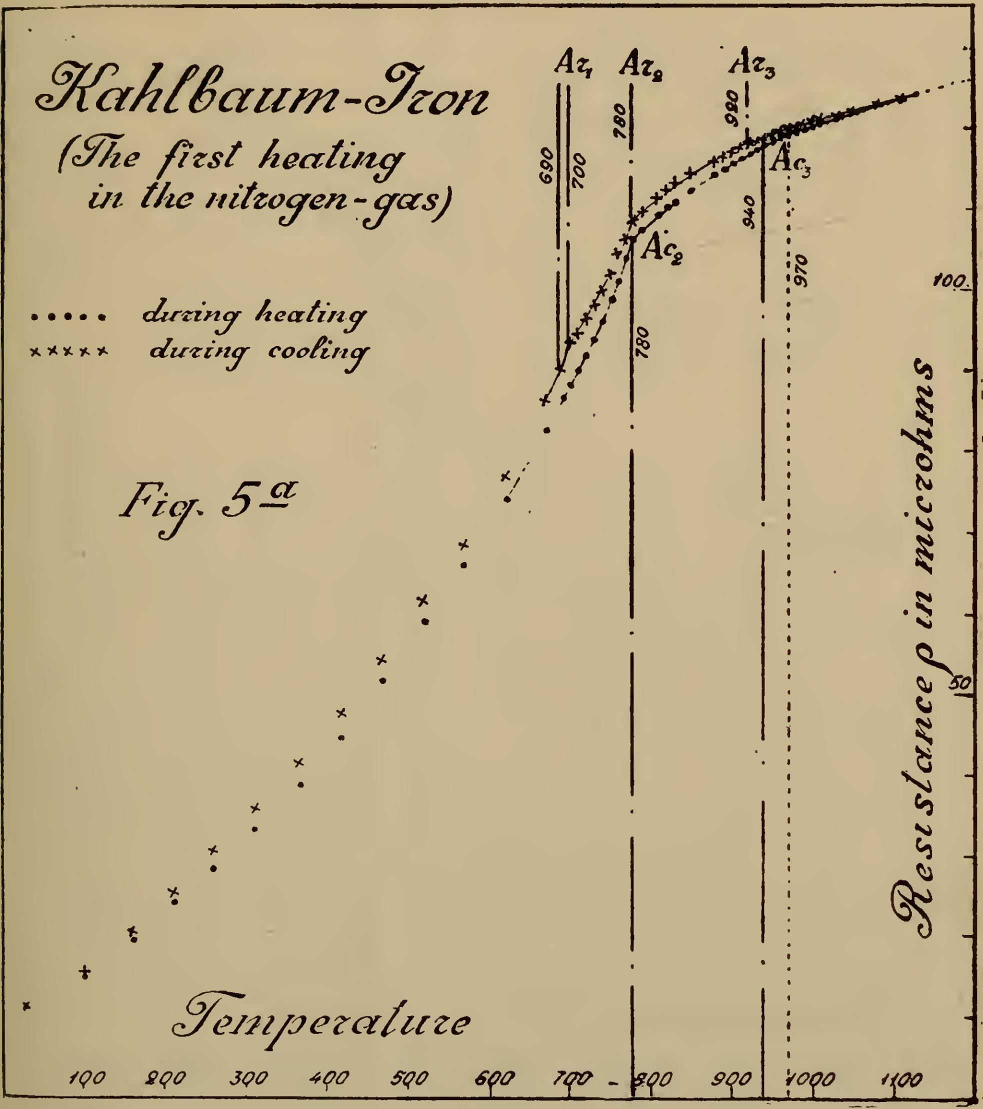
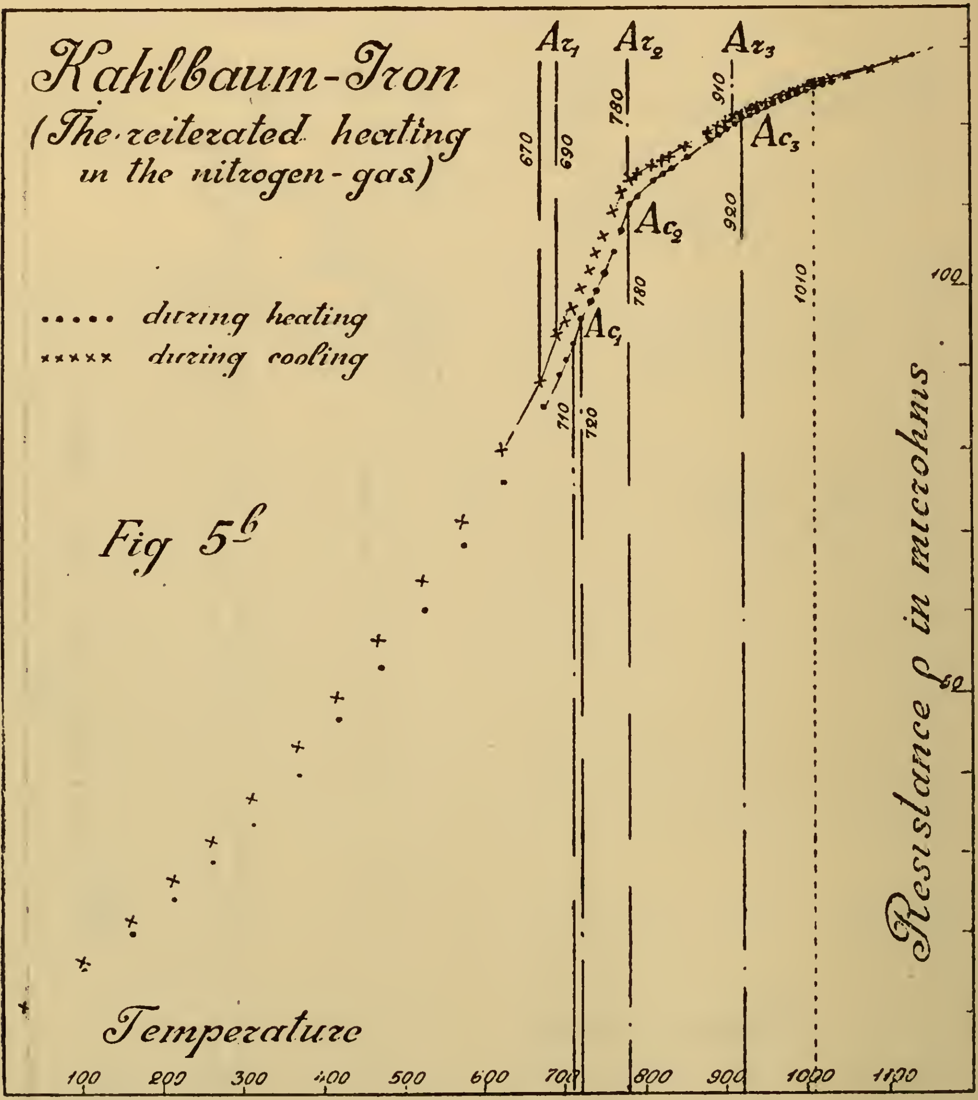


Fig. 5a

From the diagram shown in Fig. 5*a*, it is evident that in heating the Kahlbaum iron in nitrogen, the point Ac1 is absent, whereas in cooling the point Ar1 appears. The same sample was heated again in nitrogen in order to note the changes in the electric resistance of the Kahlbaum iron and the results are plotted in diagram Fig. 5*b*. The curve shows the appearance of point



Ac1 on heating. This leads to the supposition that the Kahlbaum iron has absorbed during heating a certain quantity of nitrogen, which is confirmed by the fact that the electric resistance before heating (10·527 microhms) differs somewhat from the electric resistance after heating (10·995 microhms), as shown in Table V*a*. In the same manner, the electric resistance at 1130° is much weaker at the first heating (124·660) than it is at the repeated heating (129·130 microhms).

It follows from the above that the exact position of the point Ar3 can be determined only *in vacuo*.

The observed position of the point Ar3 on the diagram, Fig. 5*a*, at 920°, and also that on diagram, Fig. 5*b*, at 910°, support the conclusion that the critical point Ar3 for pure iron lies higher than 910°. There is further to be noted the very interesting fact that the critical point A2 at 780° both before and after the change in the electric resistance, is much more clearly defined than the point A3, which hardly differs in any respect from the new point observed at 980° to 1000°.

TABLE II.

| No. | Composition. | | | | | | | Owner of the Material. |
|---|---|---|---|---|---|---|---|---|
| | C. | Mn. | Si. | P. | S. | Cu. | Total Impurities. | |
| 1. (Kahlbaum). | Not determined | | | | | | | N. S. Kurnakoff |
| 2. (electrolytic) | 0·019 | 0·025 | 0·006 | 0·012 | 0·004 | ... | 0·047 | N. S. Konstantinoff |
| 3 | 0·11 | 0·04 | 0·12 | 0·01 | 0·024 | 0·03 | 0·224 | P. Goerens |
| 4 | 0·17 | 0·01 | 0·11 | 0·01 | 0·022 | 0·03 | 0·182 | |
| 5 | 0·35 | 0·07 | 0·13 | 0·01 | 0·021 | 0·03 | 0·261 | |
| 6 | 0·45 | 0·08 | 0·13 | 0·01 | 0·021 | 0·03 | 0·271 | |
| 7 | 0·54 | 0·10 | 0·13 | 0·01 | 0·021 | 0·04 | 0·301 | |
| 8 | 0·63 | 0·07 | 0·11 | 0·01 | 0·024 | 0·03 | 0·244 | |
| 9 | 0·81 | 0·09 | 0·13 | 0·01 | 0·020 | 0·03 | 0·260 | |
| 10 | 0·89 | 0·08 | 0·12 | 0·01 | 0·021 | 0·03 | 0·261 | |
| 11 | 1·00 | 0·10 | 0·12 | 0·01 | 0·022 | 0·03 | 0·282 | |
| 12 | 1·22 | 0·12 | 0·13 | 0·01 | 0·019 | 0·03 | 0·309 | |
| 13 | 1·43 | 0·13 | 0·14 | 0·01 | 0·019 | 0·03 | 0·329 | |
| 14 | 1·54 | 0·12 | 0·15 | 0·018 | 0·014 | 0·03 | 0·322 | |

TABLE III. (*See Figs.* 5 *and* 6.)

| Temperature. | Kahlbaum Iron. | | | | Electrolytic Iron (Carbon 0·02 per Cent.). | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 10·457 | 10·920 | 9·563 | 9·158 | 10·949 | 11·484 | 9·133 | 8·708 |
| 100 | 15·084 | 15·846 | 6·630 | 6·311 | 15·466 | 16·213 | 6·466 | 6·168 |
| 150 | 17·737 | 19·893 | 5·638 | 5·027 | 20·990 | 22· | 4·764 | 4·406 |
| 200 | 20·978 | 24·310 | 4·767 | 4·114 | 24·529 | 26·847 | 4·077 | 3·725 |
| 250 | 25·210 | 28·270 | 3·967 | 3·537 | 28·190 | 31·485 | 3·547 | 3·176 |
| 300 | 29·800 | 32·772 | 3·356 | 3·051 | 32·827 | 36·489 | 3·046 | 2·741 |
| 350 | 34·933 | 38·354 | 2·863 | 2·607 | 38·196 | 41·736 | 2·618 | 2·396 |
| 400 | 41·236 | 44·116 | 2·425 | 2·267 | 44·300 | 47·106 | 2·257 | 2·123 |
| 450 | 47·988 | 50·508 | 2·084 | 1·980 | 51·010 | 53·940 | 1·960 | 1·854 |
| 500 | 54·740 | 57·621 | 1·827 | 1·735 | 57·844 | 60·894 | 1·729 | 1·642 |
| 550 | 62·123 | 64·374 | 1·610 | 1·553 | 64·800 | 67·120 | 1·543 | 1·490 |
| 600 | 70·225 | 72·027 | 1·424 | 1·388 | 72·853 | 75·784 | 1·373 | 1·320 |
| 650 | 78·510 | 80·850 | 1·274 | 1·236 | 81·274 | 84·082 | 1·231 | 1·190 |
| 680 | 83·550 | 85·712 | 1·197 | 1·167 | 86·522 | 91·524 | 1·156 | 1·093 |
| 690 | 85·442 | 87·692 | 1·170 | 1·140 | 88·110 | 95·184 | 1·135 | 1·051 |
| 700 | 87·152 | 90·032 | 1·147 | 1·111 | 89·820 | 97·382 | 1·113 | 1·027 |
| 710 | 88·862 | 94·265 | 1·125 | 1·061 | 91·890 | 99·460 | 1·088 | 1·005 |
| 720 | 90·662 | 96·334 | 1·103 | 1·038 | 93·968 | 101·409 | 1·064 | 0·986 |
| 730 | 92·464 | 98·315 | 1·082 | 1·017 | 98·850 | 104·341 | 1·012 | 0·958 |
| 740 | 94·445 | 100·300 | 1·059 | 0·997 | 101·53 | 106·415 | 0·985 | 0·940 |
| 750 | 96·514 | 102·280 | 1·036 | 0·978 | 103·73 | 108·365 | 0·964 | 0·923 |
| 760 | 98·855 | 104·260 | 1·012 | 0·959 | 105·800 | 109·830 | 0·945 | 0·910 |
| 770 | 101·380 | 106·330 | 0·986 | 0·941 | 107·270 | 111·050 | 0·932 | 0·900 |
| 780 | 104·350 | 109·030 | 0·958 | 0·917 | 108·120 | 112·150 | 0·925 | 0·892 |
| 790 | 105·520 | 110·470 | 0·948 | 0·905 | 108·850 | 112·761 | 0·919 | 0·887 |
| 800 | 106·600 | 111·730 | 0·938 | 0·895 | 109·831 | 113·371 | 0·910 | 0·882 |
| 850 | 111·910 | 116·410 | 0·894 | 0·859 | 113·492 | 116·052 | 0·881 | 0·862 |
| 880 | 114·880 | 118·580 | 0·870 | 0·843 | 115·687 | 117·400 | 0·864 | 0·852 |
| 890 | 115·960 | 119·110 | 0·862 | 0·840 | 116·178 | 117·884 | 0·861 | 0·848 |
| 900 | 117·040 | 119·650 | 0·854 | 0·836 | 116·665 | 118·375 | 0·857 | 0·845 |
| 910 | 118·120 | 120·100 | 0·847 | 0·833 | 117·273 | 118·620 | 0·853 | 0·843 |
| 920 | 119·200 | 120·660 | 0·839 | 0·829 | 117·519 | 118·983 | 0·851 | 0·840 |
| 930 | 120·200 | 121·000 | 0·832 | 0·826 | 117·884 | 119·350 | 0·848 | 0·838 |
| 940 | 121·100 | 121·270 | 0·826 | 0·825 | 118·249 | 119·592 | 0·846 | 0·836 |
| 950 | 121·360 | 121·540 | 0·824 | 0·823 | 118·620 | 119·835 | 0·843 | 0·834 |
| 980 | 122·170 | 122·260 | 0·819 | 0·818 | 119·716 | 120·691 | 0·835 | 0·829 |
| 1000 | 122·720 | 122·800 | 0·815 | 0·814 | 120·447 | 121·056 | 0·830 | 0·826 |
| 1020 | 123·250 | 123·430 | 0·811 | 0·810 | 121·183 | 121·789 | 0·825 | 0·821 |
| 1050 | 124·060 | 124·430 | 0·806 | 0·804 | 122·153 | 122·400 | 0·819 | 0·817 |
| 1080 | 124·880 | 125·300 | 0·801 | 0·798 | 123·008 | 123·131 | 0·813 | 0·812 |
| 1100 | 125·420 | ... | 0·797 | ... | 123·620 | ... | 0·809 | ... |

TABLE IV. (*See Figs. 7 and 8.*)

| Temperature. | Carbon, 0·11 per Cent. | | | | Carbon, 0·17 per Cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 12·093 | 12·545 | 8·267 | 7·971 | 12·851 | 13·064 | 7·782 | 7·639 |
| 100 | 16·872 | 17·479 | 5·925 | 5·722 | 17·597 | 18·044 | 5·683 | 5·542 |
| 150 | 20·436 | 21·070 | 4·893 | 4·746 | 20·601 | 22·022 | 4·854 | 4·541 |
| 200 | 23·395 | 24·875 | 4·274 | 4·020 | 24·012 | 25·432 | 4·165 | 3·932 |
| 250 | 27·480 | 29·315 | 3·639 | 3·411 | 27·776 | 29·340 | 3·600 | 3·408 |
| 300 | 31·710 | 33·966 | 3·153 | 2·944 | 32·181 | 33·743 | 3·107 | 2·964 |
| 350 | 37·350 | 39·463 | 2·677 | 2·534 | 37·083 | 39·356 | 2·697 | 2·541 |
| 400 | 42·916 | 45·100 | 2·330 | 2·217 | 43·334 | 45·465 | 2·307 | 2·200 |
| 450 | 49·330 | 51·442 | 2·027 | 1·944 | 49·160 | 51·715 | 2·034 | 1·937 |
| 500 | 55·671 | 58·280 | 1·796 | 1·716 | 55·554 | 58·110 | 1·800 | 1·721 |
| 550 | 62·717 | 65·325 | 1·594 | 1·531 | 62·657 | 64·787 | 1·596 | 1·544 |
| 600 | 69·905 | 72·725 | 1·431 | 1·375 | 70·260 | 72·460 | 1·423 | 1·380 |
| 650 | 78·572 | 81·180 | 1·273 | 1·232 | 78·286 | 80·840 | 1·277 | 1·237 |
| 680 | 83·928 | 86·044 | 1·191 | 1·162 | 83·544 | 86·170 | 1·197 | 1·161 |
| 690 | 85·690 | 88·158 | 1·167 | 1·135 | 85·250 | 87·946 | 1·173 | 1·137 |
| 700 | 87·382 | 91·400 | 1·144 | 1·094 | 86·882 | 90·010 | 1·151 | 1·111 |
| 710 | 89·144 | 96·190 | 1·122 | 1·039 | 88·730 | 94·481 | 1·127 | 1·058 |
| 720 | 90·976 | 98·660 | 1·099 | 1·013 | 90·434 | 96·900 | 1·106 | 1·032 |
| 730 | 93·160 | 100·980 | 1·073 | 0·990 | 92·350 | 99·315 | 1·083 | 1·007 |
| 740 | 95·630 | 103·020 | 1·046 | 0·971 | 94·840 | 101·590 | 1·054 | 0·984 |
| 750 | 98·800 | 105·000 | 1·012 | 0·952 | 98·745 | 103·790 | 1·013 | 0·964 |
| 760 | 101·470 | 106·900 | 0·986 | 0·935 | 101·440 | 105·920 | 0·986 | 0·944 |
| 770 | 103·730 | 108·660 | 0·964 | 0·920 | 103·720 | 107·840 | 0·964 | 0·927 |
| 780 | 105·770 | 110·640 | 0·945 | 0·903 | 105·850 | 109·760 | 0·945 | 0·911 |
| 790 | 107·110 | 111·900 | 0·933 | 0·894 | 107·270 | 110·750 | 0·932 | 0·903 |
| 800 | 108·380 | 112·900 | 0·923 | 0·886 | 108·550 | 111·670 | 0·921 | 0·895 |
| 850 | 112·960 | 116·420 | 0·885 | 0·859 | 112·950 | 115·650 | 0·885 | 0·865 |
| 860 | 113·810 | 117·120 | 0·879 | 0·854 | 114·310 | 116·150 | 0·875 | 0·861 |
| 870 | 114·660 | 117·820 | 0·872 | 0·848 | 115·650 | 116·646 | 0·865 | 0·857 |
| 880 | 115·570 | 118·320 | 0·865 | 0·845 | 116·510 | 117·070 | 0·858 | 0·857 |
| 890 | 116·420 | 118·600 | 0·859 | 0·843 | 117·000 | 117·427 | 0·855 | 0·852 |
| 900 | 117·050 | 118·950 | 0·854 | 0·841 | 117·356 | 117·850 | 0·852 | 0·849 |
| 920 | 118·400 | 119·730 | 0·845 | 0·835 | 118·067 | 118·420 | 0·847 | 0·844 |
| 950 | 119·800 | 120·500 | 0·835 | 0·830 | 119·210 | 119·490 | 0·839 | 0·837 |
| 980 | 121·000 | 121·630 | 0·827 | 0·822 | 120·270 | 120·410 | 0·832 | 0·831 |
| 1000 | 121·560 | 122·120 | 0·823 | 0·819 | 120·830 | 120·980 | 0·828 | 0·827 |
| 1020 | 122·400 | 122·620 | 0·817 | 0·816 | 121·550 | 121·620 | 0·823 | 0·822 |
| 1050 | 124·030 | ... | 0·806 | ... | 122·610 | ... | 0·816 | ... |

TABLE V. (*See Figs.* 9 *and* 10.)

| Temperature. | Carbon, 0·35 per Cent. | | | | Carbon, 0·45 per Cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Cooling. | During Heating. | During Heating. | During Cooling. |
| 25 | 14·636 | 14·811 | 6·833 | 6·747 | 15·333 | 15·480 | 6·522 | 6·460 |
| 100 | 19·465 | 19·935 | 5·137 | 5·016 | 20·225 | 20·388 | 4·944 | 4·905 |
| 150 | 22·783 | 23·566 | 4·389 | 4·243 | 23·301 | 24·153 | 4·291 | 4·140 |
| 200 | 25·986 | 27·766 | 3·848 | 3·602 | 27·563 | 28·273 | 3·628 | 3·537 |
| 250 | 30·045 | 31·897 | 3·328 | 3·135 | 31·683 | 32·680 | 3·156 | 3·060 |
| 300 | 34·460 | 36·453 | 2·902 | 2·743 | 36·087 | 37·864 | 2·771 | 2·641 |
| 350 | 40·511 | 42·006 | 2·468 | 2·381 | 41·345 | 43·192 | 2·419 | 2·315 |
| 400 | 46·064 | 48·200 | 2·171 | 2·075 | 47·100 | 48·875 | 2·123 | 2·046 |
| 450 | 51·831 | 54·110 | 1·929 | 1·848 | 53·142 | 54·842 | 1·881 | 1·823 |
| 500 | 58·381 | 60·660 | 1·713 | 1·649 | 59·177 | 61·662 | 1·690 | 1·622 |
| 550 | 64·930 | 67·068 | 1·540 | 1·491 | 65·924 | 67·700 | 1·517 | 1·477 |
| 600 | 73·190 | 73·703 | 1·366 | 1·357 | 73·313 | 75·160 | 1·364 | 1·331 |
| 650 | 81·380 | 82·231 | 1·229 | 1·216 | 81·696 | 83·118 | 1·224 | 1·203 |
| 680 | 86·504 | 87·288 | 1·156 | 1·146 | 86·740 | 88·160 | 1·153 | 1·134 |
| 690 | 88·284 | 89·352 | 1·133 | 1·119 | 88·310 | 89·864 | 1·132 | 1·113 |
| 700 | 90·064 | 92·272 | 1·110 | 1·084 | 89·937 | 91·711 | 1·112 | 1·094 |
| 710 | 91·844 | 99·392 | 1·089 | 1·006 | 91·500 | 100·520 | 1·093 | 0·995 |
| 720 | 93·480 | 104·090 | 1·070 | 0·961 | 93·275 | 106·560 | 1·072 | 0·938 |
| 730 | 95·402 | 106·010 | 1·048 | 0·943 | 95·190 | 108·690 | 1·051 | 0·920 |
| 740 | 97·540 | 107·930 | 1·025 | 0·926 | 97·325 | 110·610 | 1·028 | 0·904 |
| 750 | 102·740 | 110·000 | 0·973 | 0·909 | 104·290 | 112·380 | 0·959 | 0·890 |
| 760 | 107·510 | 111·780 | 0·930 | 0·895 | 109·540 | 113·660 | 0·913 | 0·880 |
| 770 | 109·640 | 112·830 | 0·912 | 0·886 | 111·460 | 114·44 | 0·897 | 0·874 |
| 780 | 111·280 | 113·980 | 0·899 | 0·877 | 112·960 | 114·800 | 0·885 | 0·871 |
| 790 | 112·630 | 114·700 | 0·888 | 0·872 | 113·820 | 115·080 | 0·879 | 0·869 |
| 800 | 113·350 | 115·190 | 0·882 | 0·868 | 114·230 | 115·440 | 0·875 | 0·866 |
| 850 | 116·190 | 117·120 | 0·861 | 0·854 | 116·360 | 117·430 | 0·859 | 0·852 |
| 880 | 117·540 | 118·320 | 0·851 | 0·845 | 117·430 | 118·710 | 0·852 | 0·842 |
| 900 | 118·250 | 118·970 | 0·846 | 0·840 | 118·140 | 119·420 | 0·847 | 0·837 |
| 920 | 118·970 | 119·610 | 0·840 | 0·836 | 118·850 | 120·06 | 0·841 | 0·833 |
| 950 | 120·180 | 120·680 | 0·832 | 0·829 | 119·920 | 120·910 | 0·837 | 0·827 |
| 980 | 121·110 | 121·530 | 0·826 | 0·823 | 120·980 | 121·760 | 0·827 | 0·821 |
| 1000 | 121·820 | 121·960 | 0·821 | 0·820 | 121·690 | 122·330 | 0·822 | 0·818 |
| 1020 | 122·530 | 122·600 | 0·816 | 0·815 | 122·400 | 122·900 | 0·817 | 0·814 |
| 1050 | 123·600 | ... | 0·809 | ... | 123·46 | ... | 0·810 | ... |

TABLE VI. (*See Figs.* 11 *and* 12.)

| Temperature. | Carbon, 0·54 per Cent. | | | | Carbon, 0·63 per Cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 16·506 | 16·657 | 6·058 | 6·004 | 16·727 | 16·558 | 5·978 | 6·180 |
| 100 | 21·421 | 21·942 | 4·668 | 4·557 | 21·617 | 22·117 | 4·626 | 7·521 |
| 150 | 25·240 | 25·671 | 3·962 | 3·895 | 25·296 | 25·850 | 3·953 | 3·865 |
| 200 | 28·110 | 29·543 | 3·557 | 3·385 | 29·029 | 29·790 | 3·445 | 3·357 |
| 250 | 31·910 | 33·702 | 3·134 | 2·967 | 33·175 | 33·522 | 3·014 | 2·983 |
| 300 | 36·283 | 38·578 | 2·756 | 2·592 | 37·807 | 38·013 | 2·645 | 2·631 |
| 350 | 42·450 | 43·884 | 2·356 | 2·279 | 43·474 | 43·612 | 2·300 | 2·293 |
| 400 | 48·330 | 49·621 | 2·069 | 2·015 | 49·420 | 49·557 | 2·024 | 2·018 |
| 450 | 53·924 | 54·496 | 1·854 | 1·835 | 55·640 | 55·845 | 1·797 | 1·791 |
| 500 | 60·593 | 61·524 | 1·650 | 1·625 | 62·273 | 62·481 | 1·606 | 1·600 |
| 550 | 66·686 | 68·983 | 1·500 | 1·450 | 69·050 | 69·323 | 1·448 | 1·443 |
| 600 | 77·720 | 76·151 | 1·338 | 1·313 | 76·511 | 76·786 | 1·307 | 1·302 |
| 650 | 82·680 | 83·252 | 1·210 | 1·201 | 84·322 | 84·664 | 1·186 | 1·181 |
| 680 | 87·626 | 88·630 | 1·141 | 1·128 | 89·300 | 89·644 | 1·120 | 1·116 |
| 690 | 89·562 | 90·210 | 1·117 | 1·109 | 90·890 | 91·302 | 1·100 | 1·095 |
| 700 | 91·212 | 91·928 | 1·096 | 1·088 | 92·614 | 93·100 | 1·080 | 1·074 |
| 710 | 92·860 | 97·162 | 1·077 | 1·029 | 94·136 | 101·670 | 1·062 | 0·984 |
| 720 | 95·082 | 107·920 | 1·052 | 0·927 | 95·794 | 110·450 | 1·044 | 0·905 |
| 730 | 96·802 | 110·640 | 1·033 | 0·904 | 97·525 | 113·210 | 1·025 | 0·883 |
| 740 | 98·452 | 112·650 | 1·016 | 0·888 | 99·460 | 115·080 | 1·006 | 0·869 |
| 750 | 103·110 | 113·940 | 0·970 | 0·878 | 108·160 | 116·250 | 0·925 | 0·860 |
| 760 | 110·570 | 114·660 | 0·904 | 0·872 | 115·570 | 116·740 | 0·865 | 0·857 |
| 770 | 112·940 | 115·230 | 0·885 | 0·868 | 116·940 | 117·150 | 0·855 | 0·854 |
| 780 | 114·150 | 115·590 | 0·876 | 0·865 | 117·360 | 117·560 | 0·852 | 0·851 |
| 790 | 114·940 | 116·020 | 0·870 | 0·862 | 117·770 | 117·980 | 0·849 | 0·848 |
| 800 | 115·380 | 116·450 | 0·867 | 0·859 | 118·190 | 118·330 | 0·846 | 0·845 |
| 850 | 117·450 | 118·460 | 0·851 | 0·844 | 120·260 | 120·400 | 0·832 | 0·831 |
| 880 | 118·460 | 119·390 | 0·844 | 0·837 | 121·440 | 121·510 | 0·824 | 0·823 |
| 900 | 119·110 | 120·110 | 0·840 | 0·833 | 122·130 | 122·220 | 0·819 | 0·818 |
| 920 | 119·890 | 120·750 | 0·834 | 0·828 | 122·410 | 122·750 | 0·817 | 0·815 |
| 950 | 121·040 | 121·780 | 0·826 | 0·821 | 123·440 | 123·720 | 0·810 | 0·808 |
| 980 | 122·040 | 122·540 | 0·819 | 0·816 | 124·410 | 124·620 | 0·804 | 0·801 |
| 1000 | 122·760 | 123·120 | 0·815 | 0·812 | 125·100 | 125·24 | 0·799 | 0·798 |
| 1020 | 123·470 | 123·690 | 0·810 | 0·808 | 125·790 | 125·93 | 0·795 | 0·794 |
| 1050 | 124·56 | ... | 0·803 | ... | 126·760 | ... | 0·782 | ... |

TABLE VII. (*See Figs.* 13 *and* 14.)

| Temperature. | Carbon, 0·81 per Cent. | | | | Carbon, 0·89 per Cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 17·790 | 17·918 | 5·621 | 5·581 | 19·309 | 19·607 | 5·179 | 5·100 |
| 100 | 22·925 | 22·976 | 4·362 | 4·352 | 24·628 | 25·042 | 4·060 | 3·993 |
| 150 | 26·227 | 27·166 | 3·813 | 3·681 | 28·835 | 28·835 | 3·468 | 3·468 |
| 200 | 29·840 | 31·068 | 3·351 | 3·294 | 32·555 | 32·984 | 3·072 | 3·032 |
| 250 | 33·741 | 35·475 | 2·964 | 2·819 | 36·704 | 37·277 | 2·724 | 2·683 |
| 300 | 38·221 | 40·100 | 2·616 | 2·494 | 41·355 | 42·143 | 2·418 | 2·373 |
| 350 | 43·567 | 44·867 | 2·295 | 2·229 | 47·080 | 47·794 | 2·124 | 2·092 |
| 400 | 49·637 | 50·792 | 2·015 | 1·969 | 52·874 | 53·446 | 1·891 | 1·871 |
| 450 | 55·271 | 56·716 | 1·809 | 1·763 | 58·670 | 59·529 | 1·704 | 1·680 |
| 500 | 61·270 | 63·580 | 1·632 | 1·573 | 65·110 | 65·824 | 1·536 | 1·519 |
| 550 | 68·060 | 70·517 | 1·469 | 1·418 | 71·548 | 72·263 | 1·398 | 1·384 |
| 600 | 75·864 | 77·164 | 1·318 | 1·296 | 78·776 | 79·776 | 1·269 | 1·254 |
| 650 | 83·740 | 84·680 | 1·194 | 1·181 | 86·574 | 87·432 | 1·155 | 1·144 |
| 680 | 88·724 | 89·734 | 1·127 | 1·114 | 90·940 | 92·440 | 1·100 | 1·082 |
| 690 | 90·530 | 91·687 | 1·105 | 1·091 | 92·440 | 93·942 | 1·082 | 1·064 |
| 700 | 92·050 | 93·350 | 1·086 | 1·071 | 94·017 | 95·446 | 1·063 | 1·048 |
| 710 | 93·855 | 101·730 | 1·065 | 0·983 | 95·660 | 107·820 | 1·045 | 0·954 |
| 720 | 95·370 | 113·360 | 1·049 | 0·882 | 97·450 | 116·690 | 1·026 | 0·857 |
| 730 | 97·032 | 114·520 | 1·031 | 0·873 | 99·310 | 117·340 | 1·007 | 0·852 |
| 740 | 99·057 | 114·880 | 1·010 | 0·871 | 101·600 | 117·770 | 0·984 | 0·849 |
| 750 | 107·290 | 115·53 | 0·932 | 0·866 | 106·250 | 118·200 | 0·941 | 0·846 |
| 760 | 114·810 | 115·880 | 0·871 | 0·863 | 117·050 | 118·630 | 0·854 | 0·843 |
| 770 | 115·530 | 116·390 | 0·866 | 0·859 | 117·550 | 118·986 | 0·851 | 0·840 |
| 780 | 115·750 | 116·830 | 0·864 | 0·856 | 117·986 | 119·410 | 0·848 | 0·837 |
| 800 | 116·470 | 117·550 | 0·859 | 0·851 | 118·840 | 120·130 | 0·841 | 0·832 |
| 850 | 118·340 | 119·570 | 0·845 | 0·836 | 120·986 | 122·210 | 0·846 | 0·818 |
| 880 | 119·430 | 120·660 | 0·837 | 0·829 | 122·277 | 122·850 | 0·818 | 0·814 |
| 900 | 120·150 | 121·310 | 0·832 | 0·824 | 123·060 | 123·780 | 0·813 | 0·808 |
| 920 | 121·020 | 122·030 | 0·826 | 0·820 | 123·780 | 124·494 | 0·808 | 0·803 |
| 950 | 122·110 | 123·040 | 0·819 | 0·813 | 124·780 | 125·500 | 0·801 | 0·797 |
| 980 | 123·410 | 123·760 | 0·810 | 0·808 | 125·856 | 126·570 | 0·795 | 0·790 |
| 1000 | 124·120 | 124·340 | 0·806 | 0·804 | 126·500 | 127·210 | 0·791 | 0·786 |
| 1020 | 124·850 | 125·210 | 0·801 | 0·799 | 127·210 | 127·930 | 0·786 | 0·782 |
| 1050 | 125·930 | ... | 0·794 | ... | 128·356 | ... | 0·779 | ... |

TABLE VIII. (*See Figs.* 15 *and* 16.)

| Temperature. | Carbon, 1·00 per Cent. | | | | Carbon, 1·22 per Cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho\times10^5$ | | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ | | Resistance, $\rho\times1$ | | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 19·091 | 18·714 | 5·238 | 5·344 | 21·011 | 21·500 | 4·759 | 4·651 |
| 100 | 24·537 | 24·580 | 4·086 | 4·069 | 26·356 | 28·350 | 3·794 | 3·527 |
| 150 | 27·898 | 28·817 | 3·584 | 3·470 | 32·053 | 33·122 | 3·120 | 3·019 |
| 200 | 31·853 | 32·418 | 3·139 | 3·085 | 36·470 | 38·320 | 2·742 | 2·610 |
| 250 | 36·162 | 36·657 | 2·765 | 2·728 | 40·600 | 43·450 | 2·462 | 2·301 |
| 300 | 40·965 | 41·177 | 2·441 | 2·429 | 45·444 | 48·293 | 2·201 | 2·071 |
| 350 | 46·474 | 46·827 | 2·152 | 2·136 | 50·574 | 53·423 | 1·977 | 1·872 |
| 400 | 52·125 | 52·838 | 1·918 | 1·893 | 55·701 | 58·408 | 1·795 | 1·712 |
| 450 | 57·916 | 58·410 | 1·727 | 1·712 | 61·400 | 63·964 | 1·629 | 1·563 |
| 500 | 64·131 | 65·120 | 1·559 | 1·536 | 67·668 | 69·733 | 1·478 | 1·434 |
| 550 | 70·981 | 71·900 | 1·409 | 1·391 | 74·078 | 76·146 | 1·350 | 1·313 |
| 600 | 78·043 | 78·540 | 1·281 | 1·273 | 81·560 | 83·482 | 1·226 | 1·198 |
| 650 | 85·954 | 86·520 | 1·164 | 1·156 | 89·750 | 91·174 | 1·114 | 1·097 |
| 680 | 90·756 | 91·392 | 1·102 | 1·094 | 94·310 | 95·946 | 1·060 | 1·042 |
| 690 | 92·312 | 93·228 | 1·083 | 1·073 | 95·878 | 97·728 | 1·043 | 1·023 |
| 700 | 93·864 | 94·642 | 1·065 | 1·057 | 97·300 | 99·580 | 1·028 | 1·004 |
| 710 | 95·632 | 99·589 | 1·046 | 1·004 | 98·890 | 114·680 | 1·011 | 0·872 |
| 720 | 97·466 | 112·300 | 1·026 | 0·891 | 100·435 | 117·740 | 0·996 | 0·849 |
| 730 | 99·305 | 116·470 | 1·007 | 0·859 | 102·214 | 118·454 | 0·978 | 0·844 |
| 740 | 101·000 | 117·380 | 0·990 | 0·852 | 104·138 | 118·956 | 0·960 | 0·841 |
| 750 | 109·190 | 117·880 | 0·916 | 0·848 | 113·968 | 119·380 | 0·877 | 0·838 |
| 760 | 116·530 | 118·300 | 0·858 | 0·845 | 118·170 | 119·810 | 0·846 | 0·835 |
| 770 | 116·890 | 118·727 | 0·856 | 0·842 | 118·454 | 120·167 | 0·844 | 0·832 |
| 780 | 117·313 | 119·150 | 0·852 | 0·839 | 118·880 | 120·590 | 0·841 | 0·829 |
| 790 | ... | ... | ... | ... | 119·380 | 121·089 | 0·838 | 0·826 |
| 800 | 118·230 | 119·930 | 0·846 | 0·834 | 119·876 | 121·516 | 0·834 | 0·823 |
| 840 | ... | ... | ... | ... | 121·730 | 122·583 | 0·821 | 0·816 |
| 850 | 120·350 | 121·697 | 0·831 | 0·822 | 122·156 | 123·440 | 0·819 | 0·810 |
| 860 | ... | ... | ... | ... | 122·510 | 123·940 | 0·816 | 0·807 |
| 870 | ... | ... | ... | ... | 122·730 | 124·300 | 0·815 | 0·805 |
| 880 | 121·764 | 122·890 | 0·821 | 0·814 | 123·154 | 124·650 | 0·812 | 0·802 |
| 900 | 122·470 | 123·600 | 0·817 | 0·809 | 123·869 | 125·220 | 0·807 | 0·799 |
| 920 | 123·250 | 124·237 | 0·811 | 0·805 | 124·580 | 125·997 | 0·803 | 0·794 |
| 950 | 124·450 | 125·082 | 0·804 | 0·799 | 125·579 | 126·860 | 0·796 | 0·788 |
| 980 | 125·365 | 125·786 | 0·798 | 0·795 | 126·786 | 127·644 | 0·789 | 0·783 |
| 1000 | 126·000 | 126·285 | 0·794 | 0·792 | 127·570 | 128·280 | 0·784 | 0·780 |
| 1020 | 126·774 | 126·920 | 0·789 | 0·788 | 128·427 | 128·927 | 0·779 | 0·776 |
| 1050 | 127·830 | ... | 0·782 | ... | 129·635 | ... | 0.771 | ... |

TABLE IX. (*See Figs.* 17 *and* 18.)

| Temperature. | Carbon, 1·43 per Cent. | | | | Carbon, 1·54 per Cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho\times10^6$ | | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ | | Resistance, $\rho\times10^6$ | | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 22·888 | 22·759 | 4·369 | 4·394 | 21·550 | 21·477 | 4·640 | 4·656 |
| 100 | 28·611 | 28·485 | 3·495 | 3·510 | 27·120 | 26·974 | 3·687 | 3·707 |
| 150 | 32·077 | 31·799 | 3·118 | 3·145 | 30·664 | 30·950 | 3·261 | 3·231 |
| 200 | 35·547 | 35·617 | 2·813 | 2·808 | 34·318 | 35·250 | 2·914 | 2·837 |
| 250 | 39·714 | 39·990 | 2·518 | 2·500 | 38·043 | 40·192 | 2·629 | 2·488 |
| 300 | 44·295 | 44·990 | 2·258 | 2·223 | 43·058 | 44·777 | 2·322 | 2·233 |
| 350 | 49·433 | 50·405 | 2·023 | 1·984 | 48·649 | 50·580 | 2·009 | 1·977 |
| 400 | 55·404 | 56·100 | 1·805 | 1·783 | 54·449 | 56·096 | 1·836 | 1·783 |
| 450 | 62·170 | 62·140 | 1·609 | 1·609 | 60·540 | 62·330 | 1·652 | 1·604 |
| 500 | 68·041 | 68·597 | 1·470 | 1·458 | 66·700 | 68·420 | 1·499 | 1·462 |
| 550 | 74·638 | 74·846 | 1·340 | 1·336 | 73·650 | 75·370 | 1·358 | 1·327 |
| 600 | 81·790 | 81·926 | 1·223 | 1·221 | 81·171 | 83·108 | 1·232 | 1·203 |
| 650 | 89·564 | 89·772 | 1·116 | 1·114 | 88·982 | 90·986 | 1·124 | 1·099 |
| 680 | 94·284 | 95·120 | 1·061 | 1·051 | 93·710 | 96·074 | 1·067 | 1·041 |
| 690 | 95·812 | 96·644 | 1·044 | 1·035 | 95·145 | 97·936 | 1·051 | 1·021 |
| 700 | 97·410 | 98·242 | 1·027 | 1·018 | 96·646 | 100·660 | 1·035 | 0·993 |
| 710 | 98·934 | 99·422 | 1·011 | 1·006 | 98·225 | 114·632 | 1·018 | 0·872 |
| 720 | 100·530 | 110·390 | 0·995 | 0·906 | 99·942 | 120·292 | 1·001 | 0·831 |
| 730 | 102·614 | 117·473 | 0·974 | 0·851 | 101·735 | 120·864 | 0·983 | 0·827 |
| 740 | 104·280 | 118·030 | 0·959 | 0·847 | 103·740 | 121·364 | 0·964 | 0·824 |
| 750 | 109·620 | 118·513 | 0·912 | 0·844 | 107·107 | 121·794 | 0·933 | 0·821 |
| 760 | 117·888 | 118·933 | 0·848 | 0·841 | 119·860 | 122·226 | 0·832 | 0·818 |
| 770 | 118·235 | 119·350 | 0·845 | 0·838 | 120·220 | 122·654 | 0·832 | 0·815 |
| 780 | 118·724 | 119·830 | 0·842 | 0·834 | 120·575 | 123·080 | 0·829 | 0·812 |
| 790 | 119·350 | 120·250 | 0·838 | 0·831 | ... | ... | ... | ... |
| 800 | 119·900 | 120·600 | 0·832 | 0·829 | 121·578 | 124·160 | 0·822 | 0·805 |
| 850 | 122·056 | 122·540 | 0·819 | 0·816 | 123·946 | 126·800 | 0·807 | 0·789 |
| 880 | 123·377 | 123·650 | 0·810 | 0·809 | 125·380 | 128·241 | 0·798 | 0·780 |
| 900 | 124·140 | 124·485 | 0·805 | 0·803 | 126·450 | 129·250 | 0·791 | 0·774 |
| 920 | 124·970 | 125·180 | 0·800 | 0·799 | 127·670 | 130·394 | 0·783 | 0·767 |
| 950 | 126·220 | 126·290 | 0·792 | 0·791 | 129·250 | 131·465 | 0·774 | 0·761 |
| 960 | 126·500 | 126·564 | 0·790 | 0·789 | 129·750 | 131·824 | 0·771 | 0·758 |
| 970 | 126·847 | 126·918 | 0·788 | 0·787 | 130·173 | 132·176 | 0·768 | 0·756 |
| 980 | 127·120 | 127·260 | 0·787 | 0·786 | 130·680 | 132·540 | 0·765 | 0·754 |
| 990 | ... | ... | ... | ... | 131·181 | 132·900 | 0·762 | 0·752 |
| 1000 | 127·680 | 127·820 | 0·783 | 0·782 | 131·609 | 133·400 | 0·760 | 0·750 |
| 1010 | ... | ... | ... | ... | 131·900 | 133·615 | 0·758 | 0·748 |
| 1020 | 128·235 | 128·373 | 0·780 | 0·779 | 132·185 | 133·830 | 0·756 | 0·747 |
| 1030 | ... | ... | ... | ... | 132·540 | 134·020 | 0·754 | 0·746 |
| 1040 | ... | ... | ... | ... | 132·975 | 134·100 | 0·752 | 0·746 |
| 1050 | 129·070 | ... | 0·775 | ... | 133·050 | 134·300 | 0·750 | 0·745 |
| 1080 | ... | ... | ... | ... | 133·900 | 134·500 | 0·746 | 0·744 |
| 1100 | ... | ... | ... | ... | 134·600 | ... | 0·743 | ... |

TABLE X. (*See Fig.* 19.)

| No. | Carbon per Cent. | Points of the Allotropic Changes of Iron and Steel. | | | | | | $Fe_3C$. | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ac3. | Ar3. | Ac2. | Ar2. | Ac1. | Ar1. | In Heating dissolves in α Iron. | In Cooling separates out from the Mixed Crystallites. |
| 1 | Kahlbaum iron | 940 | 910 | 780 | 780 | ... | $\overbrace{710\text{–}700}^{705}$ | ... | ... |
| 2 | 0·02 | 910 | 900 | 780 | 780 | $\overbrace{720\text{–}740}^{730}$ | $\overbrace{690\text{–}670}^{680}$ | ... | ... |
| 3 | 0·11 | 890 | 880 | 780 | 780 | $\overbrace{740\text{–}750}^{745}$ | $\overbrace{710\text{–}700}^{705}$ | ... | ... |
| 4 | 0·17 | 880 | 870 | 780 | 780 | $\overbrace{740\text{–}750}^{745}$ | $\overbrace{710\text{–}700}^{705}$ | ... | ... |
| 5 | 0·35 | | | 780 | | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{720\text{–}700}^{710}$ | ... | ... |
| 6 | 0·45 | ... | ... | Ac3,Ac2<br>780 | Ar3,Ar2<br>770 | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{715\text{–}700}^{708}$ | ... | ... |
| 7 | 0·54 | ... | ... | 775 | 755 | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{720\text{–}700}^{710}$ | ... | ... |
| 8 | 0·63 | ... | ... | 765 | 745 | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{720\text{–}710}^{715}$ | ... | ... |
| 9 | 0·81 | ... | ... | 760 | 720 | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{720\text{–}700}^{710}$ | ... | ... |
| 10 | 0·89 | ... | ... | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{710\text{–}700}^{705}$ | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{710\text{–}700}^{705}$ | ... | ... |
| 11 | 1·00 | ... | ... | ... | ... | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{720\text{–}700}^{710}$ | $\overbrace{740\text{–}760}^{750}$ | 740 |
| 12 | 1·22 | ... | ... | ... | ... | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{715\text{–}700}^{708}$ | 860 | 850 |
| 13 | 1·43 | ... | ... | ... | ... | $\overbrace{740\text{–}760}^{750}$ | $\overbrace{720\text{–}710}^{715}$ | 950 | 950 |
| 14 | 1·54 | ... | ... | ... | ... | $\overbrace{745\text{–}760}^{753}$ | $\overbrace{715\text{–}700}^{708}$ | 1010 | 1010 |
| | | | | | | 748 | 707 | | |

### TABLE XI. (*See Fig.* 22.)

| Carbon per Cent. | Hardened from 950°. | | Hardened from 900°. | | Hardened from 800°. | |
|---|---|---|---|---|---|---|
| | Resistance, $\rho\times10^{6}$ | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ | Resistance, $\rho\times10^{6}$ | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ | Resistance, $\rho\times10^{6}$ | Conductivity, $K=\frac{1}{\rho}\times10^{-4}$ |
| Kahlbaum iron | 12·112 | 8·256 | 11·658 | 8·577 | 11·557 | 8·652 |
| 0·11 | 13·065 | 7·654 | 12·743 | 7·847 | 12·655 | 7·902 |
| 0·17 | 13·557 | 7·376 | 13·052 | 7·661 | 12·951 | 7·722 |
| 0·35 | 17·900 | 5·587 | 17·022 | 5·874 | 16·471 | 6·071 |
| 0·45 | 20·319 | 4·922 | 19·357 | 5·166 | 18·527 | 5·398 |
| 9·54 | 22·063 | 4·532 | 21·040 | 4·753 | 20·801 | 4·808 |
| 0·63 | 22·307 | 4·483 | 20·810 | 4·805 | 20·501 | 4·878 |
| 0·81 | 28·834 | 3·468 | 27·802 | 3·597 | 23·820 | 4·198 |
| 0·89 | 32·263 | 3·099 | 31·466 | 3·178 | 29·870 | 3·348 |
| 1·00 | 31·010 | 3·225 | 29·930 | 3·341 | 28·133 | 3·555 |
| 1·22 | 36·897 | 2·710 | 35·300 | 2·833 | 32·685 | 3·060 |
| 1·43 | 37·990 | 2·632 | 36·360 | 2·751 | 33·944 | 2·946 |
| 1·54 | 44·596 | 2·242 | 43·683 | 2·289 | 39·277 | 2·546 |

TABLE VA. (*See Figs. 5a and 5b.*)

| Temperature. | Kahlbaum Iron. (On First Heating in Nitrogen Gas.) | | | | Kahlbaum Iron. (On repeated Heating in Nitrogen Gas.) | | | |
|---|---|---|---|---|---|---|---|---|
| | Resistance, $\rho \times 10$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | | Resistance, $\rho \times 10^6$ | | Conductivity, $K = \frac{1}{\rho} \times 10^{-4}$ | |
| | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. | During Heating. | During Cooling. |
| 25 | 10·527 | 10·995 | 9·499 | 9·095 | 10·995 | 11·008 | 9·095 | 9·084 |
| 100 | 14·869 | 15·526 | 6·726 | 6·441 | 15·526 | 16·496 | 6·441 | 6·062 |
| 160 | 19·694 | 20·435 | 5·077 | 4·893 | 20·360 | 21·842 | 4·912 | 4·578 |
| 210 | 24·433 | 25·174 | 4·093 | 3·972 | 24·730 | 26·803 | 4·043 | 3·731 |
| 260 | 28·875 | 30·353 | 3·463 | 3·294 | 29·024 | 31·840 | 3·445 | 3·141 |
| 310 | 33·318 | 35·539 | 3·002 | 2·814 | 33·985 | 37·020 | 2·943 | 2·701 |
| 365 | 38·501 | 41·463 | 2·598 | 2·412 | 39·390 | 43·320 | 2·539 | 2·309 |
| 415 | 44·795 | 47·757 | 2·233 | 2·094 | 76·500 | 49·460 | 2·151 | 2·022 |
| 465 | 51·829 | 54·049 | 1·930 | 1·851 | 53·380 | 56·640 | 1·873 | 1·766 |
| 520 | 59·084 | 61·454 | 1·693 | 1·628 | 60·340 | 63·900 | 1·657 | 1·565 |
| 570 | 66·043 | 68·857 | 1·514 | 1·453 | 68·120 | 71·080 | 1·502 | 1·407 |
| 620 | 74·040 | 77·000 | 1·351 | 1·299 | 76·190 | 79·960 | 1·313 | 1·251 |
| 670 | 82·926 | 86·630 | 1·206 | 1·155 | 85·740 | 88·850 | 1·166 | 1·126 |
| 690 | 87·150 | 90·330 | 1·148 | 1·107 | 89·810 | 94·480 | 1·113 | 1·059 |
| 700 | 88·700 | 93·290 | 1·128 | 1·072 | 91·880 | 95·810 | 1·088 | 1·044 |
| 710 | 90·480 | 94·400 | 1·105 | 1·059 | 94·030 | 97·140 | 1·064 | 1·030 |
| 720 | 92·250 | 96·250 | 1·084 | 1·039 | 96·250 | 100·100 | 1·039 | 0·999 |
| 730 | 94·250 | 98·100 | 1·061 | 1·019 | 98·110 | 102·180 | 1·019 | 0·979 |
| 740 | 96·700 | 99·950 | 1·034 | 1·001 | 99·960 | 104·400 | 1·001 | 0·958 |
| 750 | 99·210 | 102·180 | 1·008 | 0·979 | 102·180 | 106·618 | 0·979 | 0·938 |
| 760 | 101·800 | 104·400 | 0·982 | 0·958 | 104·840 | 109·580 | 0·954 | 0·913 |
| 770 | 104·400 | 106·620 | 0·958 | 0·938 | 107·508 | 112·392 | 0·930 | 0·890 |
| 780 | 106·020 | 108·470 | 0·943 | 0·922 | 110·321 | 113·726 | 0·906 | 0·879 |
| 790 | 107·300 | 109·800 | 0·932 | 0·911 | 111·654 | 114·023 | 0·896 | 0·877 |
| 810 | 109·280 | 111·730 | 0·915 | 0·895 | 113·579 | 114·911 | 0·880 | 0·870 |
| 820 | 110·180 | 112·540 | 0·908 | 0·889 | 114·168 | 115·576 | 0·876 | 0·865 |
| 830 | 110·910 | 113·370 | 0·902 | 0·882 | 114·911 | 116·243 | 0·870 | 0·860 |
| 850 | 112·540 | 114·770 | 0·889 | 0·871 | 116·689 | 117·650 | 0·857 | 0·841 |
| 880 | 114·610 | 116·240 | 0·873 | 0·860 | 119·206 | 119·427 | 0·839 | 0·837 |
| 890 | 115·210 | 116·540 | 0·868 | 0·858 | 119·797 | 120·094 | 0·835 | 0·833 |
| 900 | 115·730 | 116·840 | 0·864 | 0·856 | 120·300 | 120·680 | 0·831 | 0·829 |
| 910 | 116·240 | 117·130 | 0·860 | 0·854 | 120·833 | 121·280 | 0·828 | 0·825 |
| 920 | 116·700 | 117·730 | 0·857 | 0·849 | 121·425 | 121·722 | 0·824 | 0·821 |
| 930 | 117·500 | 118·020 | 0·851 | 0·847 | 121·650 | 122·092 | 0·822 | 0·819 |
| 940 | 118·020 | 118·540 | 0·847 | 0·844 | 122·170 | 122·464 | 0·818 | 0·817 |
| 950 | 118·610 | 119·130 | 0·843 | 0·839 | 122·611 | 122·834 | 0·816 | 0·814 |
| 960 | 119·130 | 119·580 | 0·839 | 0·836 | 122·981 | 123·200 | 0·813 | 0·812 |
| 970 | 119·650 | 120·100 | 0·835 | 0·833 | 123·426 | 123·649 | 0·810 | 0·809 |
| 980 | 119·880 | 120·300 | 0·834 | 0·831 | 123·871 | 124·017 | 0·807 | 0·806 |
| 990 | 120·100 | 120·680 | 0·833 | 0·829 | 124·389 | 124·463 | 0·804 | 0·803 |
| 1000 | 120·400 | 121·000 | 0·831 | 0·827 | 124·759 | 124·834 | 0·802 | 0·801 |
| 1010 | 120·680 | 121·280 | 0·829 | 0·825 | 125·129 | 125·203 | 0·799 | 0·798 |
| 1020 | ... | ... | ... | ... | 125·423 | 125·423 | 0·797 | 0·797 |
| 1030 | 121·350 | 121·650 | 0·824 | 0·822 | 125·720 | 125·720 | 0·795 | 0·795 |
| 1050 | 122·170 | 122·310 | 0·819 | 0·818 | 126·310 | 126·310 | 0·792 | 0·792 |
| 1080 | 123·200 | 123·200 | 0·812 | 0·812 | 127·420 | 127·420 | 0·785 | 0·785 |
| 1110 | 124·100 | 124·100 | 0·806 | 0·806 | 128·460 | 128·460 | 0·778 | 0·778 |
| 1130 | 124·660 | ... | 0·802 | ... | 129·130 | ... | 0·774 | ... |

# PRESERVATION OF IRON AND STEEL BY MEANS OF PASSIVIFYING FACTORS.

By THOS. G. THOMPSON (University of Washington, Seattle, U.S.A.)

## Passivity.

When iron is immersed in solutions of chromic acid or potassium dichromate[1] for a few hours, treated with concentrated nitric acid or made the anode of an electric circuit in certain electrolytes, it becomes very inert. This phenomenon is known as passivity. Thus, for example, if a piece of iron or steel be placed in a solution of copper sulphate for a brief period, metallic copper will deposit upon the surface. If, however, the iron has been "passivified" by immersion in potassium dichromate or concentrated nitric acid, this reaction will not take place until the passivity has been destroyed. A further test for passivity is found in the fact[2] that the iron will not dissolve in nitric acid having a specific gravity of 1·20. Should iron be placed in concentrated nitric acid, the metal will begin to go into solution rapidly and then suddenly all chemical action will cease. Upon applying the above tests it will be found that the iron is in the passive state. If iron be made the positive electrode and placed in certain electrolytes and the amount of current flowing is sufficient, it will be noted that the iron will not go into solution according to Faraday's law. The iron will be passivified, the rate of solution reduced to a minimum, and bubbles of oxygen will arise from the anode.

Many explanations of this peculiar phenomenon have been offered, and the subject has claimed the attention of a vast number of investigators. No really satisfactory explanation, generally acceptable and capable of explaining the passive condition of metals under all circumstances, has, however, ever been advanced. Many investigators are supporters of the so-called oxide and gaseous film theories. A complete bibliography of the literature relating to passivity up to 1907 is given by Heathcote[1] and by Byers.[2] A symposium, "The Passivity of Metals," published by the Faraday Society in 1913, gives outlines of the more recent work upon this subject. A very clear and comprehensive chapter, "The Passive State of Iron," is given by J. Newton Friend in his interesting book, "The Corrosion of Iron and Steel."

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[1] Dunstan and Hill (*Jour. Chem. Soc.*, vol. 99, pp. 1833–53) have demonstrated that many other salts besides the dichromates may be utilised as passivifying agents.

[2] Heathcote, *Jour. Soc. Chem. Ind.*, 1907, vol. 26, p. 899.

That other metals besides iron may be rendered passive has been pointed out from time to time by various investigators. Thus Dunstan and Hill[3] describe means for producing the passive state of zinc, together with a number of other metals. The effect of potassium dichromate upon zinc, when used as a galvanising agent, will be discussed in the experimental portion of this Report.

## Passivity and its Relation to the Corrosion of Iron and Steel.

### *Passivifying Agents as Pigments.*

Although the phenomenon of passivity has been known since 1794, no real attempt was made until quite recently to make use of this peculiar fact as a means for preventing or inhibiting the corrosion of iron and steel. In 1895 M. P. Wood[4] called attention to the valuable properties possessed by insoluble and basic chromates when used as protective coatings for iron and steel. The use of such materials, when properly applied, has been strongly confirmed by all investigators in this particular field. The work of Cushman has done much to demonstrate the value of chrome pigments.

### *Soluble Passivifying Agents in Steam Boilers.*

The corrosion of steam boilers takes place under conditions very different from those of the ordinary corrosion of iron and steel. The gases dissolved in the boiler water at atmospheric temperatures are rapidly removed, to a very large extent, upon heating, thereby decreasing the relative corrosivity of the water. However, other factors are present that will stimulate corrosion within the boiler. Briefly, these are the lack of homogeneity of the boiler plates, contact of the plates with dissimilar metals, the effect of strains, and the influence of dissolved salts. The nature of these dissolved salts determine to a great extent the corrosive action that goes on within the boiler.

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[1] Heathcote, *Jour. Soc. Chem. Ind.*, 1907, vol. 26, p. 899.

[2] *Jour. Am. Chem. Soc.*, 1908, vol. 30, p. 1718.

[3] *Jour. Chem. Soc.*, vol. 99, *pp.* 1853–67.

[4] *Trans. Am. Soc. Mech. Eng.*, vol. 16, p. 671.

From the work of Grave [1] and Moseley [2] it might be concluded that the chemical composition of the boiler plates, their lack of homogeneity, and the effect of strains would have very little to do with the ease with which the plates could be passivified.

The use of soluble chromates, such as potassium dichromate, as a means for preventing corrosion in boilers was first recommended by Cushman.[3] He suggested the use of 5 lbs. of potassium dichromate to 1500 gallons of water. When this was tried on a commercial basis, it was found that the potassium dichromate had practically no influence in limiting corrosion. Archbutt [4] found that when potassium dichromate was added to the concentrated boiler water, corrosion was not prevented, "especially in locomotive boilers where metallic copper is in contact with the boiler." The exact nature of the dissolved salts was not stated. Friend and Brown [5] have studied the effect of potassium dichromate and potassium chromate in varying concentrations in a number of solutions of sodium chloride ranging from fairly dilute to saturated. Tests were run for a few days at room temperature and at 95° C. With the potassium dichromate in sodium chloride corrosion took place readily both in the cool and hot solutions; and it was found that corrosion increased with the increase in concentration of the dichromate. However, with potassium chromate, increase in concentration of this salt in the presence of the sodium chloride caused decrease in the rate of corrosion. The point at which corrosion was practically eliminated corresponded with the presence of an amount of dichromate which would have cost so much on a commercial basis as to make its application prohibitive. The tests of Friend and Brown at 95° were continued for just three days, and during that time the solutions were heated only twelve hours a day, the solutions being allowed to cool to room temperature over night. While this treatment stimulated corrosive action, the results do not represent the true action of sodium chloride and potassium dichromate at 95° C.

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[1] *Z. physik. Chem.*, vol. 77, pp. 513–76.

[2] *Jour. Am. Chem. Soc.*, 1915, vol. 37, pp. 2326–34.

[3] *United States Department of Agriculture, Office of Public Roads, Bulletin* No. 30.

[4] *Engineering*, vol. 93, p. 824.

[5] *Journal of the Iron and Steel Institute*, 1911, No. I. p. 125.

As the great majority of boiler waters are practically free from chlorides, it seems probable that corrosion would be inhibited in waters containing sulphates alone if the water were treated with proper amounts of potassium dichromate. No quantitative data has yet been secured with mixed solutions of varying strengths of sulphates and potassium dichromate. Cushman [1] has shown qualitatively that with the increase of copper sulphate in solutions containing uniformly small amounts of potassium dichromate, the rate at which the copper was deposited was increased.

### *Anodic Passivity.*

The possibility of making a boiler the anode in an electric circuit was suggested by Byers and Voris.[2] They were able to keep iron passive when it was used as an anode and placed in an electrolyte consisting of sodium chloride and potassium dichromate, there being forty times as much potassium dichromate as sodium chloride. The electrolyte was heated so that a pressure of from 20 to 50 lbs. per square inch was obtained. As there are so many factors that would tend to destroy this passivity in an ordinary steam boiler, it therefore seems very doubtful whether this form of passivity would be of any real practical value. With the increase in concentration of the boiler water, the increase in the amount of the potassium dichromate would have to be forty times that of the sodium chloride, and this very fact would render the cost of operation impossible. No work has yet been done showing the effect of the dichromate with the various sulphates commonly found in boiler waters, when the iron or boiler is made the anode in an electric circuit.

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[1] Cushman and Gardner, "Corrosion and Preservation of Iron and Steel," p. 113.

[2] *Jour. Am. Chem. Soc.*, 1912, vol. 34, pp. 1368–79.

## Purpose of this Research.

Since the corrosion problem is so vast in extent, the author has limited himself to studying the means for preventing corrosion in steam boilers and receptacles for containing water for purely industrial purposes. The object of this research is to study the effect of various passivifying agents upon the rate of corrosion of different grades of iron in solutions of salts commonly occurring in boiler waters. The experimental work may be divided into four parts :

*First :* To ascertain the effect of varying amounts of potassium dichromate in solutions of different concentrations of sodium chloride, sodium sulphate, calcium sulphate, magnesium chloride, and magnesium sulphate at room temperature and at the temperature of boiling water.

Since the publication of the suggestion of the use of potassium dichromate as a means for preventing boiler corrosion, many text-books have been published which mention the use of potassium dichromate as a preventive for corrosion. It is the aim of the author to present sufficient data to establish definitely the truth or fallacy of this statement.

*Second :* To determine the efficiency of di-sodium phosphate as an inhibitive agent, the samples of iron and steel being placed in the above-mentioned solutions.

*Third :* To secure data regarding the action of zinc or galvanised iron in various solutions of sodium chloride and sodium sulphate containing varying amounts of potassium dichromate.

*Fourth :* To determine the practicability of keeping iron passive with potassium dichromate in the presence of the salts characteristic of boiler waters, when the iron is made the anode in an electric circuit and heated to a pressure varying from 120 lbs. to 150 lbs. per square inch.

## Experimental.

### *The Nature and Preparation of the Samples of Iron and Steel.*

The test-pieces used in all the following experiments consisted of a commercially pure iron and a low carbon steel, both of which had been rolled into sheets. The author is indebted to the American Rolling-Mill Company of Middletown, Ohio, who kindly supplied him with samples of their manufacture. The following shows the composition of the test-pieces :

| | Commercially Pure Iron. Per Cent. | Low Carbon Steel. Per Cent. |
|---|---|---|
| Carbon | 0·012 | 0·112 |
| Phosphorus | 0·004 | 0·045 |
| Silicon | 0·001 | 0·003 |
| Sulphur | 0·017 | 0·052 |
| Manganese | 0·015 | 0·388 |

For the corrosion tests, plates having a surface of 42 square centimetres were cut from the sheets, the plates being 8 cm. × $2\frac{1}{2}$ cm. After cutting, a small hole was punched at the top of each plate so that it could be attached to a thread and suspended in solution. The plates were then numbered and pickled in a solution of dilute sulphuric acid until all foreign matter was removed and they were bright in appearance. The acid was removed by washing rapidly and thoroughly in water and then treating with alcohol, ether, and finally with gasoline. After the latter had evaporated from the surfaces of the plates by holding them over a source of indirect heat, they were placed in desiccators containing calcium chloride and eventually weighed.

## *Preparation of Solutions.*

Normal solutions of sodium chloride, sodium sulphate, magnesium chloride, and magnesium sulphate, and a saturated solution of calcium sulphate at 20° C. were made. From the first four solutions, N/10, N/100, and N/1000 solutions were prepared. A solution of potassium dichromate containing 100 grammes of the salt per litre and a normal solution of di-sodium phosphate were also made. Small amounts of these solutions were measured into the bottles in which the individual corrosion tests were to be run, so that when the other solutions were introduced they would also contain either a thousandth or a hundredth part of an equivalent weight of potassium dichromate or sodium phosphate. Amounts of these two latter substances were weighed out and placed in the various solutions so that they gave strengths of either N/10 or N/5.

In mentioning the normality of a potassium dichromate solution no reference is meant to its oxidising power. A normal solution of the dichromate is considered here as containing half the gramme molecular weight.

### *Apparatus.*

In running the corrosion tests at room temperature, one plate was placed in each bottle. The bottles were of 300 cubic centimetres capacity, and were arranged in such a manner as to permit the passage of a slow stream of air through the solution. The arrangement is shown in the accompanying illustration, Fig. 1, where *a* is the tube through which the air passes, *b* the test-plate, suspended by means of a thin silk thread, which is held in place at the outlet tube, *c*, by means of a rubber. Five of these bottles

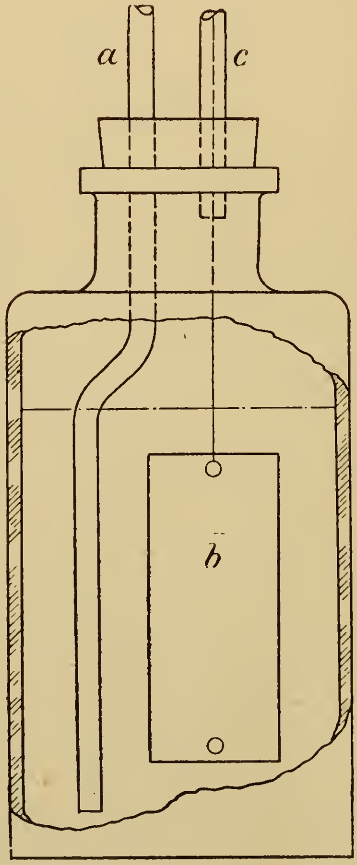

Fig. 1.

were placed in series without the slight increase in pressure in the first few bottles having any effect upon the rate of corrosion. The outlet tube *c* was so far above the surface of the solution that any danger of particles of the liquid being carried over into the next bottle was practically eliminated.

The apparatus used for determining the rate of corrosion at the temperature of boiling water consisted of three large tin-plated tubs, in which the bottles containing the individual test-plates were placed. The illustration, Fig. 2, shows the arrangement of one of the water-baths. These tubs were heated by means of gas-burners, the water being supplied by means of a constant levelling device shown at *a* and $a_1$. Two of these levelling devices were utilised for each tub, so that an accident to one would prevent the water from boiling away during the night. Water entered the apparatus at *b*, and the excess ran off through the tube *c*. The bottles containing the plates were stoppered with wooden plugs, which had previously been steamed and then wrapped with tinfoil. These plugs were loosely fitted in order that the volume of gases could regulate itself without difficulty upon heating. A wooden rack supported the bottles within the tub. A cover, with a few small holes for the escape of steam, fitted securely over the top of the apparatus.

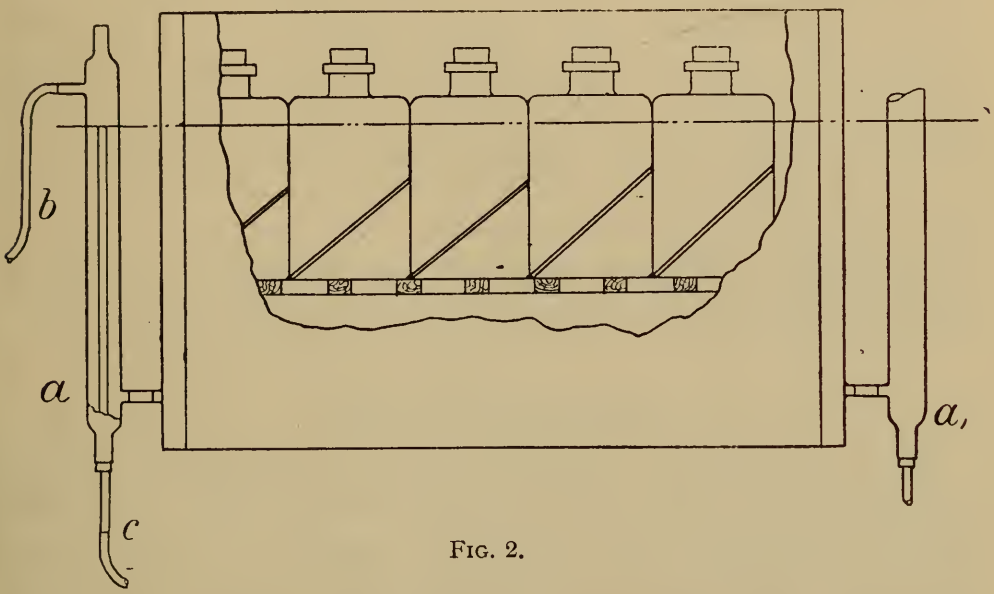

FIG. 2.

### *Conditions under which the Tests were Run.*

In order to promote corrosion, should it occur, as rapidly as possible at room temperature, air was slowly bubbled through the solutions. The air was thoroughly washed in a series of wash bottles and permitted to pass through the solutions ten hours every day. This produced two important factors, namely, keeping the solutions saturated with oxygen and insuring the homogeneity of the liquids by constant stirring. All the tests were performed in a laboratory free from direct sunlight.

The bottles used to contain the solutions and test-plates for treatment at 100° C. were subjected to the action of boiling water for twenty hours a day for two weeks, before they were utilised for running the corrosion tests. During this time they were removed each day from the tub, emptied, cooled, and washed, then refilled and returned to the tub. The test-plates were not suspended in the solutions but were laid diagonally across the lower end of the bottle, with just the four corners touching the sides.

### *Cleaning the Test-Plates.*

The rust which had collected on the test-plates run at room temperature was removed by treatment with either ammonium citrate or dilute sulphuric acid. Ammonium citrate, after treatment for a little time, removed the rust from the plates immersed in solutions containing no potassium dichromate or sodium phosphate, or very small amounts of these substances. Sulphuric acid had to be resorted to in order to remove the rust formed on some of the plates which had been in solutions containing N/10 and N/5 dichromate. In cases of this nature the rust was always in the form of hard minute spots. With the solutions containing the larger amounts of sodium phosphate, the corrosive material was of a peculiar nature, it being a dull green colour which always occurred in the form of streaks or large spots on the metal. These streaks and spots could be easily removed by gently rubbing with the fingers. After cleaning and washing the plates were dried in the manner previously described.

With the tests run at the temperature of boiling water it was impossible to clean the plates. Long immersions in ammonium citrate for two and three days had no desirable effect. On the other hand, if the plates were treated with sulphuric acid, part of the very thin scaly material covering the plate would be removed while the remainder would still be intact, and before this could be removed portions of the exposed metal would begin to dissolve. After a number of various attempts to clean these plates, it was finally decided, after washing with water and alcohol and drying, to weigh them directly. In the great majority of cases, no test for iron was obtained in the solutions, and thus weighing, without cleaning, probably gave fairly accurate results.

The spots occurring on the plates after immersion in the hot solutions containing potassium dichromate were invariably of black or brownish-black colour. Those in solutions containing larger amounts of sodium phosphate were of the characteristic dull green colour.

## ACTION OF SOLUTIONS OF CHLORIDES AND SULPHATES UPON IRON AND STEEL AT ROOM TEMPERATURE IN THE PRESENCE OF POTASSIUM DICHROMATE.

The following results show the effect of various amounts of potassium dichromate upon the rate of corrosion of iron and steel when introduced into solutions of different concentrations of chlorides and sulphates. In some cases the addition of dichromate prevented corrosion completely, especially with the more concentrated solutions of this substance, while in others its inhibiting character was very striking.

When placed in solutions free from dichromate, the low carbon steel showed a slightly greater tendency toward corrosion than did the commercially pure iron.

Test-plates of the low carbon steel and the commercially pure iron were placed in distilled water and subjected to the same treatment as accorded to the samples in the various solutions. The results thus obtained were utilised as a standard in computing the relative corrosion. This was determined by taking the loss in weight of the samples in the distilled water and dividing into the loss in weight by the test-plates in the solutions.

$$\text{Relative corrosion} = \frac{\text{Loss in weight in X solution.}}{\text{Loss in weight in distilled water.}}$$

## Commercially Pure Iron. Room Temperature.

### Table I.—*Action of Water.*

| No. | Original Weight. | Loss in Weight. | Remarks. |
|---|---|---|---|
| A | 18·4197 | 0·1995 | Badly corroded. |
| B | 19·6435 | 0·2021 | ,, ,, |
| C | 16·6748 | 0·1969 | ,, ,, |
| D | 19·2308 | 0·1956 | ,, ,, |

### Table II.—*Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 81 | 1/1000 | 19·8732 | 0·0010 | 0 | Slight corrosion on edges. |
| 82 | 1/100 | 18·8425 | 0·0004[1] | 0 | No corrosion. |
| 83 | 1/10 | 18·9613 | 0·0000 | 0 | Metal bright. |
| 84 | 1/5 | 18·0086 | 0·0001 | 0 | ,, ,, |

## Low Carbon Steel. Room Temperature.

### Table III.—*Action of Water.*

| No. | Original Weight. | Loss in Weight. | Remarks. |
|---|---|---|---|
| A | 7·3013 | 0·2232 | Badly corroded. |
| B | 7·8240 | 0·2113 | ,, ,, |
| C | 8·0327 | 0·2135 | ,, ,, |
| D | 7·9241 | 0·2203 | ,, ,, |

### Table IV.—*Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 329 | 1/1000 | 8·4997 | 0·0005 | 0 | Slight corrosion. |
| 330 | 1/100 | 8·1320 | 0·0001 | 0 | No corrosion. |
| 331 | 1/10 | 8·1652 | 0·0003 | 0 | Metal bright. |
| 332 | 1/5 | 8·0663 | 0·0004 | 0 | ,, ,, |

[1] Gain in weight.

## COMMERCIALLY PURE IRON. ROOM TEMPERATURE.

### TABLE V.—*Sodium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 1 | 1/1000 | 18·2439 | 0·2298 | 115 | Covered with rust. |
| 2 | 1/100 | 19·8746 | 0·2203 | 110 | ,, ,, ,, |
| 3 | 1/10 | 20·1324 | 0·1897 | 93 | ,, ,, ,, |
| 4 | N | 20·4938 | 0·1204 | 59 | ,, ,, ,, |

### TABLE VI.—*Sodium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 5 | 1/1000 | 20·4132 | 0·2133 | 105 | Covered with rust. |
| 6 | 1/100 | 19·5453 | 0·2175 | 107 | ,, ,, ,, |
| 7 | 1/10 | 19·7463 | 0·2556 | 128 | ,, ,, ,, |
| 8 | N | 19·7077 | 0·1561 | 78 | ,, ,, ,, |

### TABLE VII.—*Magnesium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 9 | 1/1000 | 19·0452 | 0·2028 | 103 | Covered with rust. |
| 10 | 1/100 | 18·7933 | 0·2468 | 122 | ,, ,, ,, |
| 11 | 1/10 | 20·4995 | 0·1686 | 83 | ,, ,, ,, |
| 12 | N | 19·5231 | 0·1214 | 55 | ,, ,, ,, |

### TABLE VIII.—*Magnesium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 13 | 1/1000 | 19·8018 | 0·2283 | 113 | Covered with rust. |
| 14 | 1/100 | 20·3402 | 0·1828 | 90 | ,, ,, ,, |
| 15 | 1/10 | 20·2853 | 0·1258 | 62 | ,, ,, ,, |
| 16 | N | 19·2753 | 0·1176 | 58 | ,, ,, ,, |

## Low Carbon Steel. Room Temperature.

### Table IX.—*Sodium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 249 | 1/1000 | 8·0917 | 0·2597 | 119 | Covered with rust. |
| 250 | 1/100 | 7·8634 | 0·2267 | 104 | ,, ,, ,, |
| 251 | 1/10 | 7·4396 | 0·1648 | 75 | ,, ,, ,, |
| 252 | N | 7·5003 | 0·1124 | 52 | ,, ,, ,, |

### Table X.—*Sodium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 253 | 1/1000 | 7·9239 | 0·2285 | 105 | Covered with rust. |
| 254 | 1/100 | 7·9880 | 0·2332 | 108 | ,, ,, ,, |
| 255 | 1/10 | 7·7302 | 0·2505 | 115 | ,, ,, ,, |
| 256 | N | 7·4951 | 0·1786 | 82 | ,, ,, ,, |

### Table XI.—*Magnesium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 257 | 1/1000 | 7·0276 | 0·2640 | 122 | Covered with rust. |
| 258 | 1/100 | 7·8348 | 0·2832 | 130 | ,, ,, ,, |
| 259 | 1/10 | 8·0051 | 0·1562 | 72 | ,, ,, ,, |
| 260 | N | 8·1704 | 0·1137 | 52 | ,, ,, ,, |

### Table XII.—*Magnesium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 261 | 1/1000 | 8·1027 | 0·2529 | 116 | Covered with rust. |
| 262 | 1/100 | 7·6020 | 0·2670 | 122 | ,, ,, ,, |
| 263 | 1/10 | 7·9926 | 0·2218 | 102 | ,, ,, ,, |
| 264 | N | 7·4304 | 0·1893 | 87 | ,, ,, ,, |

## COMMERCIALLY PURE IRON. ROOM TEMPERATURE.

### TABLE XIII.—*Sodium Sulphate with* N/1000 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 17 | 1/1000 | 17·7931 | 0·0190 | 10 | Corrosion around edges. |
| 18 | 1/100 | 17·4386 | 0·0165 | 8 | ,, ,, ,, |
| 19 | 1/10 | 18·8439 | 0·0077 | 4 | Few small rust spots. |
| 20 | N | 17·5677 | 0·0132 | 7 | ,, large ,, |

### TABLE XIV.—*Sodium Sulphate with N*/100 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 21 | 1/1000 | 18·8235 | 0·0000 | 0 | No rust. |
| 22 | 1/100 | 17·9828 | 0·0005 | 0 | ,, ,, |
| 23 | 1/10 | 17·8812 | 0·0021 | 1 | Few minute rust spots. |
| 24 | N | 18·5079 | 0·0046 | 2 | Rust around edges. |

### TABLE XV.—*Sodium Sulphate with N*/10 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 25 | 1/1000 | 17·7866 | 0·0001 [1] | 0 | Metal bright. No rust. |
| 26 | 1/100 | 18·6974 | 0·0005 [1] | 0 | ,, ,, ,, |
| 27 | 1/10 | 18·5133 | 0·0006 [1] | 0 | Several black spots. |
| 28 | N | 18·1652 | 0·0043 | 2 | ,, ,, ,, |

### TABLE XVI.—*Sodium Sulphate with N*/5 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 29 | 1/1000 | 18·6887 | 0·0001 [1] | 0 | Metal bright. No rust. |
| 30 | 1/100 | 18·9888 | 0·0002 [1] | 0 | ,, ,, ,, |
| 31 | 1/10 | 18·4944 | 0·0003 | 0 | Several minute spots. |
| 32 | N | 18·5613 | 0·0045 | 2 | Many minute rust spots. |

[1] Gain in weight.

## LOW CARBON STEEL. ROOM TEMPERATURE.

### TABLE XVII.—*Sodium Sulphate with N*/1000 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 265 | 1/1000 | 8·0241 | 0·0112 | 5 | Few rust spots. |
| 266 | 1/100 | 7·0198 | 0·0225 | 10 | ,, ,, |
| 267 | 1/10 | 8·4727 | 0·0090 | 4 | ,, ,, |
| 268 | N | 7·9607 | 0·0092 | 4 | ,, ,, |

### TABLE XVIII.—*Sodium Sulphate with N*/100 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 269 | 1/1000 | 6·7617 | 0·0001 | 0 | No corrosion. |
| 270 | 1/100 | 6·7436 | 0·0033 | 2 | Few rust spots. |
| 271 | 1/10 | 7·7283 | 0·0032 | 2 | ,, ,, |
| 272 | N | 7·9914 | 0·0045 | 2 | ,, ,, |

### TABLE XIX.—*Sodium Sulphate with N*/10 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 273 | 1/1000 | 6·6671 | 0·0001 | 0 | No corrosion. |
| 274 | 1/100 | 6·2877 | 0·0000 | 0 | ,, ,, |
| 275 | 1/10 | 6·7019 | 0·0067 | 3 | Few rust spots. |
| 276 | N | 8·4086 | 0·0049 | 2 | ,, ,, |

### TABLE XX.—*Sodium Sulphate with N*/5 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 277 | 1/1000 | 6·9826 | 0·0003 | 0 | No corrosion. |
| 278 | 1/100 | 6·9373 | 0·0001 | 0 | ,, ,, |
| 279 | 1/10 | 6·9747 | 0·0010[1] | 0 | ,, ,, |
| 280 | N | 6·7125 | 0·0027 | 1 | Few rust spots. |

[1] Gain in weight.

Fig. 3 illustrates the action of solutions of sodium sulphate upon commercially pure iron in the presence of varying amounts of potassium dichromate. Practically the same graph would be obtained upon plotting the data from the low carbon steel. The variation in the chemical composition of the iron and steel appears to have no influence when immersed in solutions containing potassium dichromate and sodium sulphate.

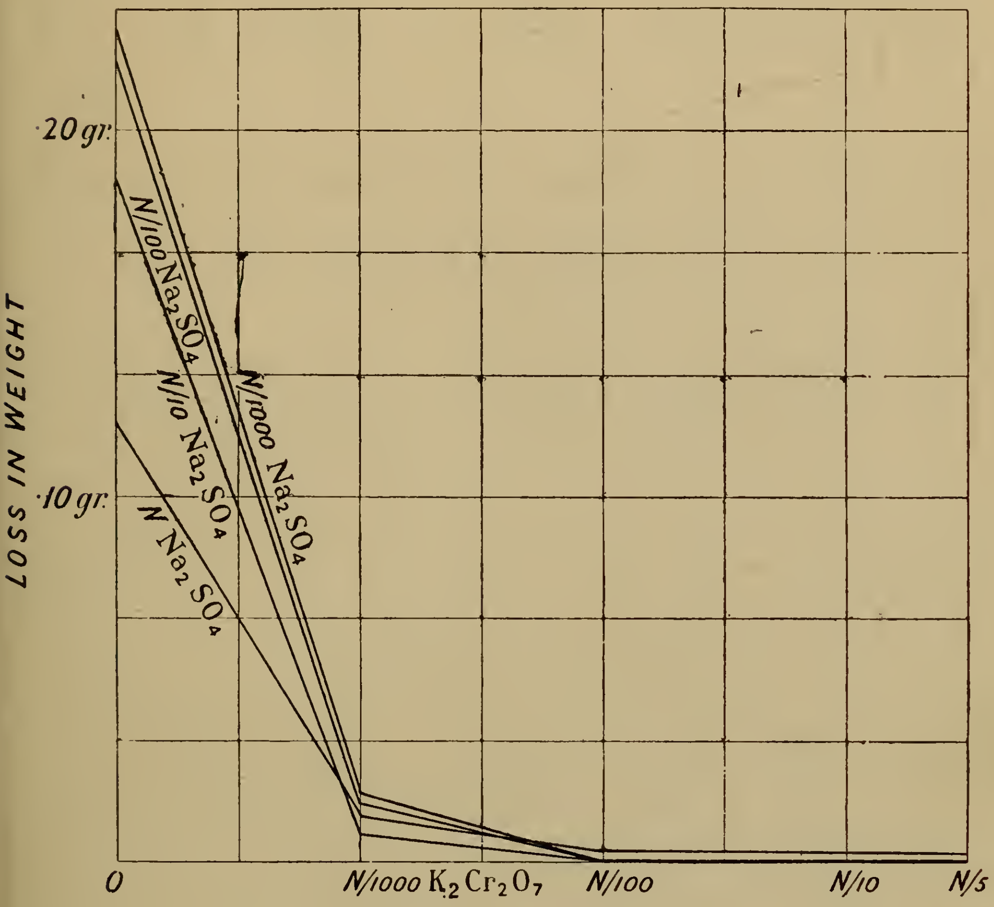

FIG. 3.

Only the solutions which contained very dilute amount of potassium dichromate showed very marked corrosion.

N/10 and N/5 dichromate rendered the iron and the steel passive in the more dilute solutions of sodium sulphate, while it greatly inhibited corrosion in the N/10 and normal solutions. The passivification of the test-plates was determined by dipping into nitric acid of 1·20 specific gravity.

## Commercially Pure Iron. Room Temperature.

Table XXI.—*Magnesium Sulphate with N/*1000 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 33 | 1/1000 | 18·6374 | 0·0011 | 1 | Slight rusting on edge. |
| 34 | 1/100 | 17·7247 | 0·0031 | 2 | ,, ,, ,, ,, |
| 35 | 1/10 | 18·5333 | 0·0080 | 4 | Many small rust spots. |
| 36 | N | 18·8740 | 0·0119 | 6 | ,, ,, ,, ,, |

Table XXII.—*Magnesium Sulphate with N/*100 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 37 | 1/1000 | 18·8471 | 0·0002[1] | 0 | No rust. |
| 38 | 1/100 | 18·7850 | 0·0022 | 1 | Several black spots. |
| 49 | 1/10 | 18·2635 | 0·0107 | 5 | Many small spots. |
| 40 | N | 18·1070 | 0·0264 | 13 | Covered with spots. |

Table XXIII.—*Magnesium Sulphate with N/*10 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 41 | 1/1000 | 18·6751 | 0·0000 | 0 | Metal bright. |
| 42 | 1/100 | 18·7850 | 0·0003[1] | 0 | ,, ,, |
| 43 | 1/10 | 18·7790 | 0·0008 | 1 | Minute rust spots. |
| 44 | N | 19·8571 | 0·0280 | 14 | Covered with spots. |

Table XXIV.—*Magnesium Sulphate with N/*5 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 45 | 1/1000 | 19·1785 | 0·0000 | 0 | Metal bright. |
| 46 | 1/100 | 19·5526 | 0·0003[1] | 0 | ,, ,, |
| 47 | 1/10 | 19·9281 | 0·0010 | 1 | Few minute rust spots. |
| 48 | N | 18·2517 | 0·0238 | 12 | Covered with rust spots. |

[1] Gain in weight.

## Low Carbon Steel. Room Temperature.

Table XXV.—*Magnesium Sulphate with N/*1000 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 281 | 1/1000 | 6·9384 | 0·0038 | 2 | Few spots over surface. |
| 282 | 1/100 | 7·0442 | 0·0127 | 6 | Many small spots. |
| 283 | 1/10 | 7·6038 | 0·0073 | 4 | Few small rust spots. |
| 284 | N | 7·6373 | 0·0124 | 6 | Many small spots. |

Table XXVI.—*Magnesium Sulphate with N/*100 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 285 | 1/1000 | 7·7890 | 0·0000 | 0 | No corrosion. |
| 286 | 1/100 | 7·7853 | 0·0050 | 3 | Few rust spots. |
| 287 | 1/10 | 7·9115 | 0·0094 | 5 | " " " |
| 288 | N | 7·6104 | 0·0218 | 11 | Many rust spots. |

Table XXVII.—*Magnesium Sulphate with N/*10 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 289 | 1/1000 | 7·5233 | 0·0002 | 0 | No corrosion. |
| 290 | 1/100 | 7·8860 | 0·0001 | 0 | " " |
| 291 | 1/10 | 8·1318 | 0·0004 | 0 | " " |
| 292 | N | 7·6104 | 0·0210 | 11 | Covered with spots. |

Table XXVIII.—*Magnesium Sulphate with N/*5 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 293 | 1/1000 | 7·4765 | 0·0002 | 0 | Metal bright. |
| 294 | 1/100 | 7·2624 | 0·0002 | 0 | " " |
| 295 | 1/10 | 8·1285 | 0·0007 | 0 | No corrosion. |
| 296 | N | 8·3027 | 0·0241 | 12 | Covered with rusty spots. |

Fig. 4 shows the effect of solutions of magnesium sulphate upon commercially pure iron in the presence of different concentrations of potassium dichromate. If the data obtained by the action of these solutions upon low carbon steel were similarly plotted practically the same graph would result. This would indicate that the impurities and differences in the physical characteristics of the test-plates have no influence upon the action of the potassium dichromate.

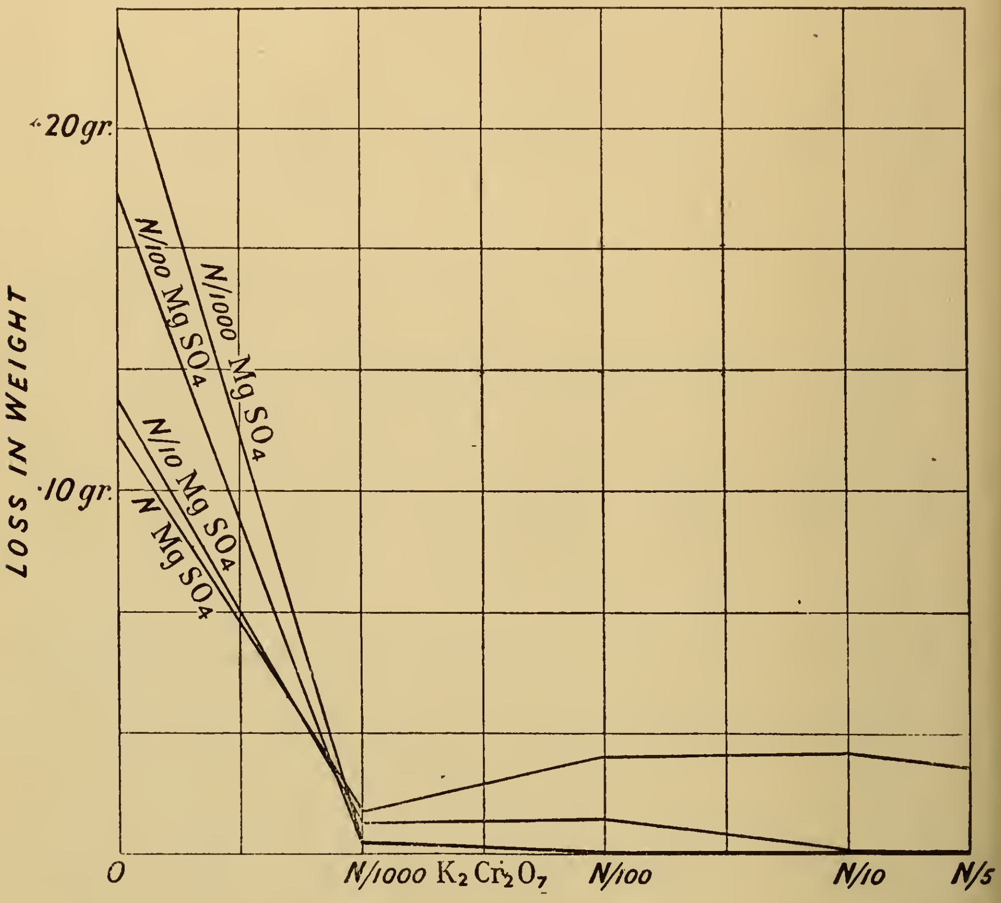

Fig. 4.

N/1000 dichromate added to the magnesium sulphate solutions caused distinct corrosion (Tables XXI. and XXV.). N/10 and normal magnesium sulphate containing dichromate in all proportions were covered with rust spots of varying sizes. While this was generally true in the case of the sodium sulphate solutions, the rate of corrosion with the magnesium sulphate was much greater.

N/10 and N/5 dichromate passivified the test-plates of both the iron and the steel in N/1000 magnesium sulphate. This was also the case with N/5 dichromate in N/100 magnesium sulphate. However, with N/10 dichromate in the latter solutions the passive state was demonstrated twice out of four test-plates of iron and twice with three test-plates of steel.

To determine the passive state of the iron and steel, other plates than those used to secure the loss in weight were run under identical conditions. At the end of two weeks they were washed carefully, and then immersed in the nitric acid of 1·20 specific gravity.

### COMMERCIALLY PURE IRON. ROOM TEMPERATURE.

TABLE XXIX.—*Saturated Solution of Calcium Sulphate* (20° C.).

| No. | Normality.[1] | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 85 | 1/1000 | 18·3412 | 0·0098 | 5 | Several large streaks. |
| 86 | 1/100 | 18·0028 | 0·0007 [2] | 0 | Black spots. |
| 87 | 1/10 | 18·7949 | 0·0003 [2] | 0 | No corrosion. |
| 88 | 1/5 | 18·7370 | 0·0002 [2] | 0 | ” ” |

### LOW CARBON STEEL. ROOM TEMPERATURE.

TABLE XXX.—*Saturated Solution of Calcium Sulphate* (20° C.).

| No. | Normality.[1] | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 365 | 1/1000 | 8·0091 | 0·0088 | 4 | Minute spots. |
| 366 | 1/100 | 7·7364 | 0·0001 | 0 | No corrosion. |
| 367 | 1/10 | 7·1023 | 0·0004 | 0 | ” ” |
| 368 | 1/5 | 7·4972 | 0·0005 | 0 | ” ” |

With the exception of N/1000 dichromate, the addition of this salt to saturated calcium sulphate solutions produced results similar to those obtained in solutions containing only dichromate.

[1] Normality of potassium dichromate.
[2] Gain in weight.

## Commercially Pure Iron. Room Temperature.

### Table XXXI.—*Sodium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 49 | 1/1000 | 18·2921 | 0·0452 | 23 | Covered with rust. |
| 50 | 1/100 | 18·3231 | 0·0100 | 5 | Narrow long black streaks. |
| 51 | 1/10 | 18·5411 | 0·0122 | 6 | ,, ,, ,, ,, |
| 52 | N | 18·2830 | 0·0173 | 9 | Covered with thin layer of rust. |

### Table XXXII.—*Sodium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 53 | 1/1000 | 17·3569 | 0·0004 [1] | 0 | No corrosion. |
| 54 | 1/100 | 17·7729 | 0·0021 | 1 | Several rust spots. |
| 55 | 1/10 | 18·8033 | 0·0183 | 9 | Covered with thin layer of rust. |
| 56 | N | 18·1411 | 0·0329 | 17 | Covered with rust spots. |

### Table XXXIII.—*Sodium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 57 | 1/1000 | 17·9824 | 0·0004 [1] | 0 | No corrosion. |
| 58 | 1/100 | 18·9423 | 0·0003 [1] | 0 | ,, ,, |
| 59 | 1/10 | 18·8458 | 1·0307 | 15 | Covered with layer of rust. |
| 60 | N | 18·7504 | 0·0633 | 32 | ,, ,, ,, ,, |

### Table XXXIV.—*Sodium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 61 | 1/1000 | 17·5235 | 0·0001 [1] | 0 | Metal bright. |
| 62 | 1/100 | 18·4591 | 0·0004 [1] | 0 | ,, ,, |
| 63 | 1/10 | 17·9659 | 0·0423 | 21 | Many small rust spots. |
| 64 | N | 18·2212 | 0·0530 | 27 | Badly corroded. |

[1] Gain in weight.

## LOW CARBON STEEL. ROOM TEMPERATURE.

### TABLE XXXV.—*Sodium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 297 | 1/1000 | 8·0472 | 0·0374 | 19 | Rust spots and streaks. |
| 298 | 1/100 | 8·2619 | 0·0185 | 9 | Many rust spots. |
| 299 | 1/10 | 7·7362 | 0·0156 | 8 | Large rust spots. |
| 300 | N | 8·5746 | 0·0190 | 10 | ,, ,, ,, |

### TABLE XXXVI.—*Sodium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 301 | 1/1000 | 8·6156 | 0·0001 | 0 | No corrosion. |
| 302 | 1/100 | 7·5995 | 0·0002 | 0 | Several minute spots. |
| 303 | 1/10 | 8·5122 | 0·0174 | 9 | Many small rust spots. |
| 304 | N | 8·1990 | 0·0375 | 19 | Covered with large rust spots. |

### TABLE XXXVII.—*Sodium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 305 | 1/1000 | 8·4199 | 0·0007 | 0 | No corrosion. |
| 306 | 1/100 | 8·5453 | 0·0016 | 1 | Few minute rust spots. |
| 307 | 1/10 | 7·9314 | 0·0336 | 17 | Covered with small spots. |
| 308 | N | 8·7001 | 0·0652 | 33 | ,, ,, ,, ,, |

### TABLE XXXVIII.—*Sodium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 309 | 1/1000 | 8·0314 | 0·0005 | 0 | No corrosion. |
| 310 | 1/100 | 6·6100 | 0·0035 | 2 | Few minute spots. |
| 311 | 1/10 | 7·5867 | 0·0409 | 20 | Many large rust spots. |
| 312 | N | 8·1445 | 0·0515 | 26 | ,, ,, ,, ,, |

The behaviour of iron and steel in mixed solutions of sodium chloride and potassium dichromate is shown in Fig. 5. The two types of samples gave generally similar results.

The most peculiar action was obtained with N/1000 solution of both the sodium chloride and the dichromate. In this solution the rate of corrosion was many times higher than that obtained with magnesium chloride or the sulphates. With the commercially pure iron four tests gave a loss in weight of 0·0452, 0·0397, 0·0190, and 0·0432 gramme.

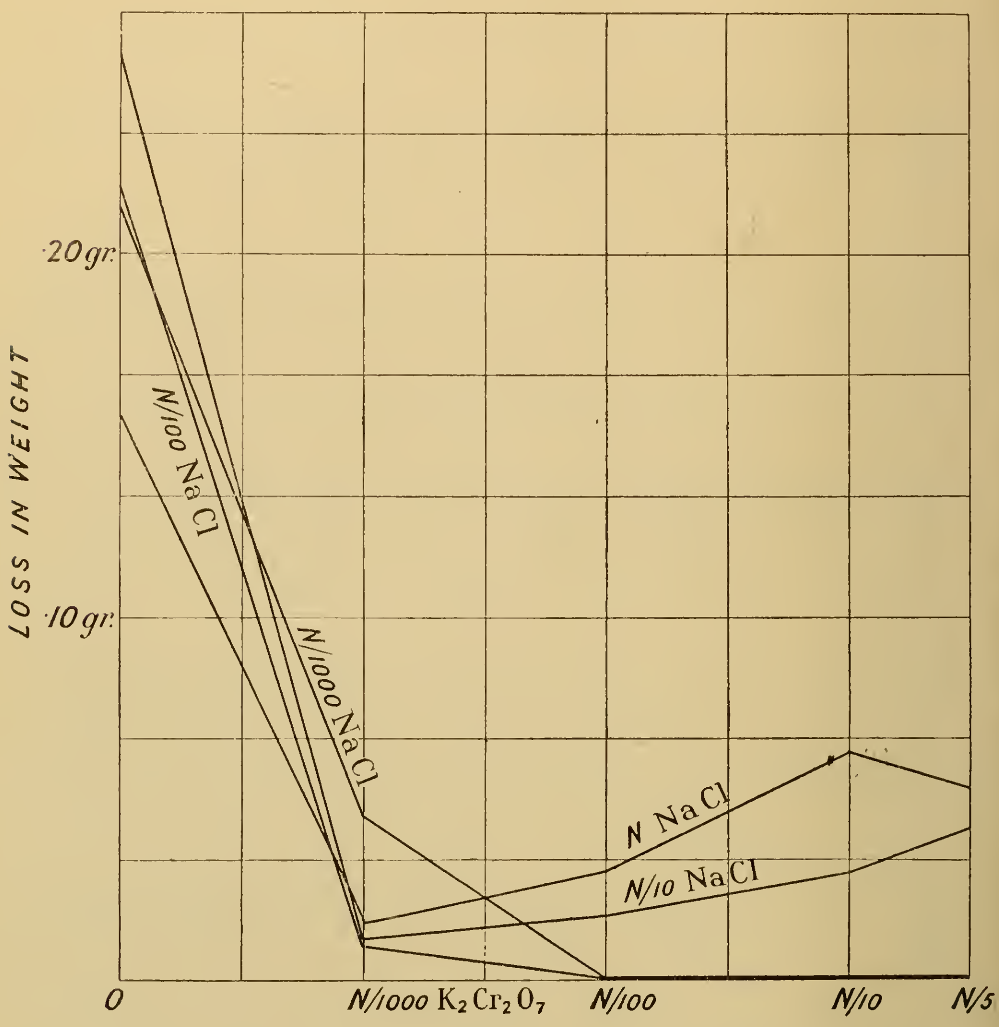

Fig. 5.

In the N/1000 and N/100 solutions of sodium chloride containing N/5 dichromate, the plates were all in the passive condition.

However, with those containing only a N/10 dichromate in N/100 sodium chloride, the plates were not all passivified, one of iron and the other of steel reacted instantly with the nitric acid.

The inhibiting action of the potassium dichromate was less in solutions of the chlorides than in solutions of corresponding concentrations of the sulphates. The loss of weight due to corrosion of commercially pure iron in solutions of magnesium chloride and potassium dichromate, as shown in Fig. 6, seems to be almost the same as that in sodium chloride solutions. The exceptions were the normal magnesium chloride solutions, which showed a greater tendency to react with both the iron and the steel.

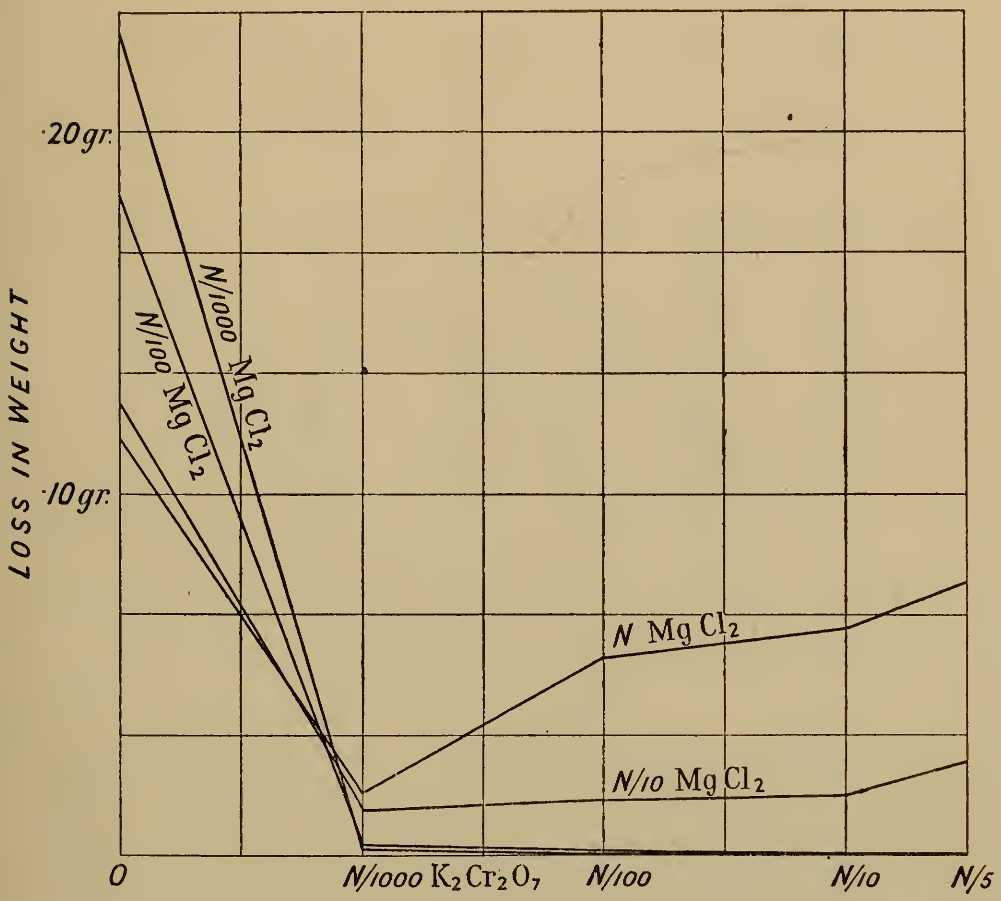

FIG. 6.

The more dilute solutions of magnesium chloride containing large amounts of dichromate produced passivity in most cases.

## Commercially Pure Iron. Room Temperature.

### Table XXXIX.—*Magnesium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 65 | 1/1000 | 17·5235 | 0·0018 | 1 | Corrosion on edges. |
| 66 | 1/100 | 18·4563 | 0·0024 | 1 | Few minute rust spots. |
| 67 | 1/10 | 18·6983 | 0·0164 | 8 | Covered with minute rust spots. |
| 68 | N | 18·8969 | 0·0128 | 6 | Many small rust spots. |

### Table XL.—*Magnesium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 69 | 1/1000 | 17·0475 | 0·0002 | 0 | Several minute spots. |
| 70 | 1/100 | 17·3322 | 0·0009 [1] | 0 | No corrosion. |
| 71 | 1/10 | 17·3590 | 0·0151 | 8 | Covered thin layer rust. |
| 72 | N | 17·8621 | 0·0246 | 12 | ,, ,, ,, ,, |

### Table XLI.—*Magnesium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 73 | 1/1000 | 19·5877 | 0·0004 [1] | 0 | Metal bright. |
| 74 | 1/100 | 18·1777 | 0·0003 [1] | 0 | ,, ,, |
| 75 | 1/10 | 18·0645 | 0·0209 | 10 | Covered with small lumpy rust spots. |
| 76 | N | 18·1682 | 0·0528 | 26 | ,, ,, ,, |

### Table XLII.—*Magnesium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 77 | 1/1000 | 18·9682 | 0·0004 [1] | 0 | Metal bright. |
| 78 | 1/100 | 17·4384 | 0·0002 [1] | 0 | ,, ,, |
| 79 | 1/10 | 18·3128 | 0·0212 | 11 | Covered with small lumpy spots. |
| 80 | N | 17·9440 | 0·0540 | 27 | ,, ,, ,, |

---

[1] Gain in weight.

## LOW CARBON STEEL. ROOM TEMPERATURE.

### TABLE XLIII.—*Magnesium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 313 | 1/1000 | 8·7930 | 0·0020 | 1 | Few rust spots. |
| 314 | 1/100 | 8·4156 | 0·0038 | 2 | ,, ,, ,, |
| 315 | 1/10 | 8·5263 | 0·0143 | 7 | Rust around edges. |
| 316 | N | 7·4669 | 0·0160 | 8 | Many minute spots. |

### TABLE XLIV.—*Magnesium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 317 | 1/1000 | 8·7930 | 0·0020 | 1 | Minute spots. |
| 318 | 1/100 | 8·3371 | 0·0057 | 3 | Several large black spots. |
| 319 | 1/10 | 7·7715 | 0·0142 | 7 | Covered with minute spots. |
| 320 | N | 8·2331 | 0·0550 | 27 | ,, ,, ,, ,, |

### TABLE XLV.—*Magnesium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 321 | 1/1000 | 7·7367 | 0·0004 | 0 | No corrosion. |
| 322 | 1/100 | 8·0481 | 0·0004 | 0 | ,, ,, |
| 323 | 1/10 | 8·0177 | 0·0193 | 10 | Covered with spots. |
| 324 | N | 8·5306 | 0·0632 | 31 | Badly corroded. |

### TABLE XLVI.—*Magnesium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 325 | 1/1000 | 7·9113 | 0·0003 | 0 | No corrosion. |
| 326 | 1/100 | 8·1286 | 0·0001 | 0 | ,, ,, |
| 327 | 1/10 | 7·9591 | 0·0259 | 13 | Covered with rust spots. |
| 328 | N | 8·3277 | 0·0756 | 38 | Badly corroded. |

## SUMMARY OF RESULTS. (ROOM TEMPERATURE.)

### *Solutions of Sodium Sulphate and Potassium Dichromate.*

1. The difference in chemical composition and physical properties had no influence upon the rate of corrosion of the iron and steel.

2. N/10 and N/5 dichromate rendered the iron and steel passive in the more dilute solutions of the sulphate.

3. In all other cases dichromate inhibited corrosion to a very marked extent.

### *Solutions of Magnesium Sulphate and Potassium Dichromate.*

1. The difference in chemical composition and physical properties had no influence upon the rate of corrosion of the iron and steel.

2. Plates immersed in N/10 and normal magnesium sulphate with all proportions of dichromate were more or less covered with rust spots.

3. In all cases dichromate inhibited corrosion to a very marked extent.

4. Test-plates showed more of a tendency toward corrosion than when placed in solutions of corresponding concentration of sodium sulphate.

5. Passive state existed on most of the plates in solutions of N/10 and N/5 dichromate with the more dilute magnesium sulphate.

### *Solutions of Calcium Sulphate and Potassium Dichromate.*

1. With the exception of N/1000 dichromate the solutions behaved as if dichromate was the only salt present.

### *Solutions of Sodium Chloride and Potassium Dichromate.*

1. Behaviour of the iron and steel appears to be the same.

2. Passive state demonstrated in many cases with N/1000 and N/100 sodium chloride containing N/10 and N/5 dichromate.

3. In the more concentrated solutions of sodium chloride an increase in either this salt or the dichromate produced an increase in the rate of corrosion.

4. The inhibiting action of the dichromate is less than that in corresponding sulphate solutions.

5. N/1000 sodium chloride with the same concentration of dichromate acted upon the iron and steel more rapidly than other solutions in this ratio.

### *Solutions of Magnesium Chloride and Potassium Dichromate.*

1. Behaviour of the iron and steel appears to be the same in many cases.

2. Test-plates were passivified in N/1000 and N/100 solutions of the chloride with N/10 and N/5 dichromate.

3. In the more concentrated solutions of the chloride, an increase in either the salt or the dichromate produces an increase in the rate of corrosion.

4. Inhibiting action of the dichromate is less than in the corresponding sulphate solutions.

5. Behaviour of many of the magnesium chloride solutions were similar to those of sodium chloride. Normal solutions of the former, however, were exceptions, corrosion being much greater.

## ACTION OF SOLUTIONS OF CHLORIDES AND SULPHATES UPON IRON AND STEEL AT THE TEMPERATURE OF BOILING WATER IN THE PRESENCE OF POTASSIUM DICHROMATE.

In the tests run at room temperature potassium dichromate reduced corrosion to a marked extent in every case, in some instances preventing all chemical action upon the iron and steel. Thus tanks used for storing non-potable waters at atmospheric temperatures could be well preserved by the addition of small quantities of potassium dichromate. However, with waters in boilers the addition of this compound will, in many cases, serve as a stimulative agent rather than as a preventive for corrosion. This will be seen by studying the data obtained when the iron and steel were placed in solutions free from dichromate at boiling temperature for two weeks and comparing them with the results from those boiled in solutions in which this salt was present. In many of the solutions the presence of the dichromate was occasioned by a slight increase in corrosion. This was especially true in the chloride solutions. In fact, from the general appearances of the test-plates, this increase in corrosion seemed greater than that actually represented by the following figures.

Plates of the iron and steel were introduced into distilled water and subjected to the same treatment as accorded to the samples in the various solutions. At the end of two weeks the plates were removed, dried, and weighed. The plates were all slightly tarnished. The gain in weight of the plates served as a standard for calculating the relative corrosion.

The test-plates immersed in the salt solutions free from dichromate corroded to a certain extent, a small brown precipitate settling on the bottom of the containing vessel. It was thus impossible to weigh the plates directly and determine the rate of corrosion by gain in weight. The plates, however, were very easily cleaned with ammonium citrate and the loss in weight determined. The equivalent amount of ferric oxide represented by the loss in weight was calculated. While this does not accurately represent the actual amount of corrosive matter produced it is fairly approximate, so that it can be reasonably compared with the data obtained from plates where cleaning was impossible.

In the graphic portrayal of the results showing the gain in weight sustained by the commercially pure iron and the low carbon steel when placed in sulphate and chloride solutions containing varying amounts of dichromate, a scale ten times as great as that employed for plotting the data at room temperature was used. Owing to the decided difference in the behaviour of the two samples, all the data obtained was plotted. The dotted lines represent the low carbon steel and the continuous lines the commercially pure iron.

Figs. 7 and 8 show the behaviour of solutions of sodium and magnesium sulphate respectively. N/5 dichromate produced a decrease in the rate of corrosion in nearly every case. In some instances, especially with solutions of sodium sulphate containing N/10 dichromate, there is a decided increase in corrosion, while in others the dichromate appears to have little or no effect. In general the addition of dichromate to boiler waters would be of no practical use, as an alteration in the concentrations of the salts would produce a difference in action. This would be especially true if chlorides were present. Under such circumstances the addition of greater amounts of dichromate to decrease the corrosive

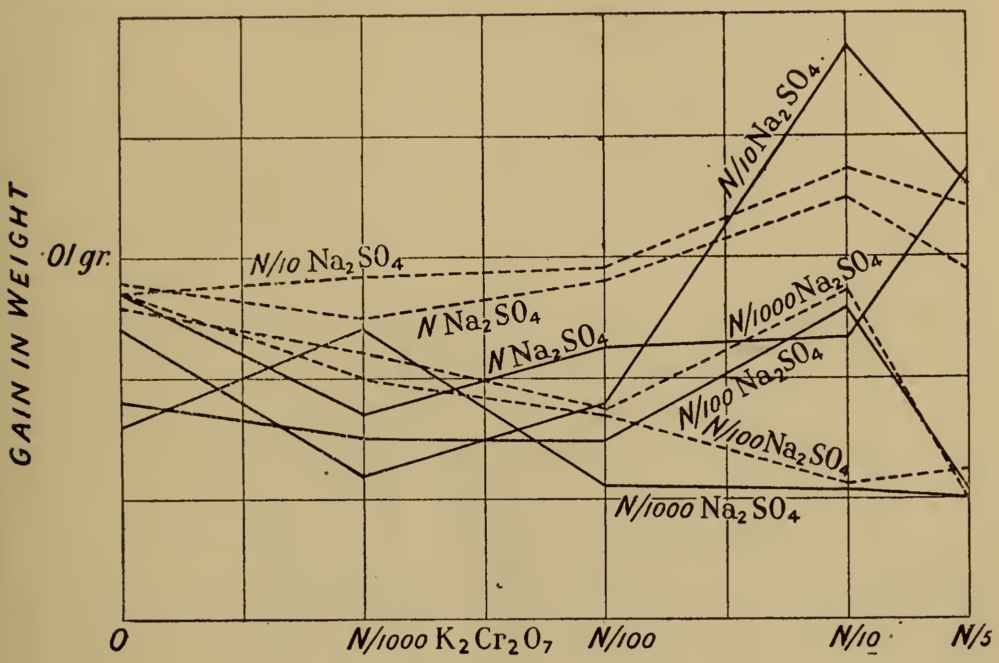

FIG. 7.

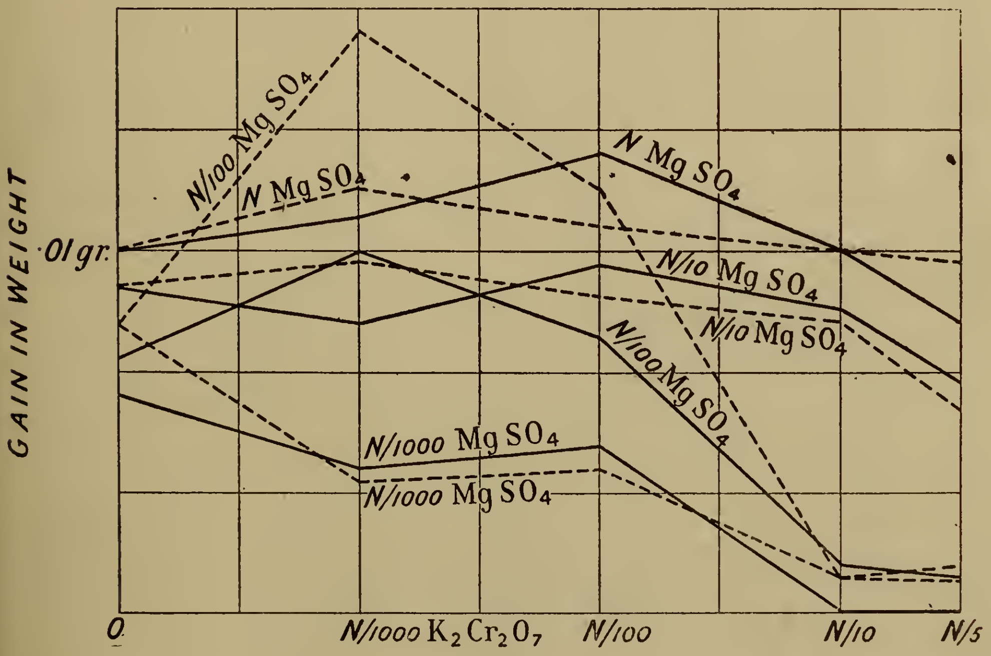

FIG. 8.

effect of the sulphates would be acted upon by the chlorides and the final result would be a stimulation of corrosion.

The presence of dichromate in solutions of the chlorides caused a decided increase in the rate of corrosion, the magnesium chloride being more violent in its behaviour than the sodium chloride. Figs. 9 and 10 illustrate the action of the chlorides upon the iron and steel. Chemical interaction undoubtedly takes place between the chlorides, potassium dichromate, and water, with the production

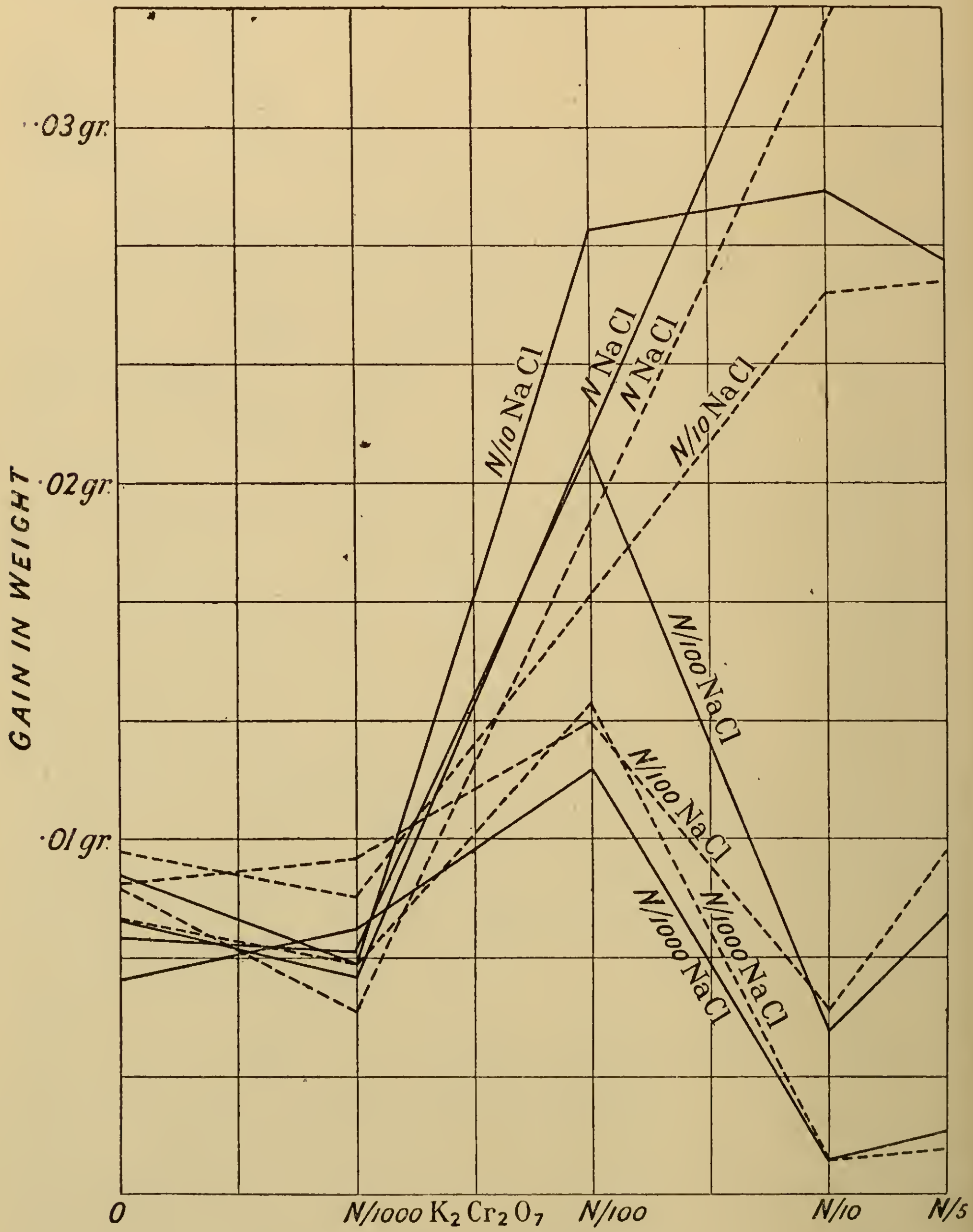

Fig. 9.

of small amounts of hydrochloric acid, thus causing the great increase in corrosive action. Friend[1] has suggested the following chemical equation to show the production of the hydrochloric acid :

$$2NaCl + K_2Cr_2O_7 + H_2O \rightarrow Na_2CrO_4 + K_2CrO_4 + 2HCl.$$

Because of experimental difficulties the results reported for the action of the stronger solutions of the chlorides with N/10 and N/5 dichromate upon the iron and steel are low.

### COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

#### TABLE XLVII.—*Action of Water.*

| No. | Original Weight. | Gain in Weight. | Remarks. |
|---|---|---|---|
| A | 19·1064 | 0·0055 | Tarnished. |
| B | 18·8200 | 0·0048 | " |
| C | 18·8349 | 0·0043 | " |
| D | 19·1126 | 0·0063 | " |
| E | 18·7442 | 0·0057 | " |

#### TABLE XLVIII.—*Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 189 | 1/1000 | 19·1515 | 0·0023 | ... | Tarnished. |
| 190 | 1/100 | 19·7182 | 0·0015 | ... | Slightly tarnished. |
| 191 | 1/10 | 18·2635 | 0·0013 | ... | " " |
| 192 | 1/5 | 19·6910 | 0·0010 | ... | " " |

### LOW CARBON STEEL. TEMPERATURE OF BOILING WATER.

#### TABLE XLXIX.—*Action of Water.*

| No. | Original Weight. | Gain in Weight. | Remarks. |
|---|---|---|---|
| A | 7·0429 | 0·0074 | Minute spots. |
| B | 7·0774 | 0·0074 | " " |
| C | 7·4627 | 0·0081 | " " |
| D | 6·9830 | 0·0090 | " " |

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[1] *Carnegie Scholarship Memoirs*, 1911.

### TABLE L.—*Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 445 | 1/1000 | 6·2030 | 0·0017 | ... | Slightly tarnished. |
| 446 | 1/100 | 7·4011 | 0·0007 | ... | ,, ,, |
| 447 | 1/10 | 6·6794 | 0·0015 | ... | ,, ,, |
| 448 | 1/5 | 7·0553 | 0·0015 | ... | ,, ,, |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### TABLE LI.—*Sodium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 193 | 1/1000 | 19·2936 | 0·0039 | 0·0056 | ... |
| 194 | 1/100 | 18·6913 | 0·0043 | 0·0061 | ... |
| 195 | 1/10 | 18·4841 | 0·0057 | 0·0081 | ... |
| 195 | N | 16·6731 | 0·0062 | 0·0089 | ... |

### TABLE LII.—*Magnesium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 197 | 1/1000 | 17·4416 | 0·0043 | 0·0061 | ... |
| 198 | 1/100 | 19·6567 | 0·0049 | 0·0070 | ... |
| 199 | 1/10 | 18·6475 | 0·0062 | 0·0089 | ... |
| 200 | N | 18·9933 | 0·0071 | 0·0101 | ... |

### TABLE LIII.—*Sodium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 201 | 1/1000 | 18·8491 | 0·0043 | 0·0061 | ... |
| 202 | 1/100 | 16·3931 | 0·0051 | 0·0073 | ... |
| 203 | 1/10 | 17·9781 | 0·0063 | 0·0090 | ... |
| 204 | N | 16·9963 | 0·0054 | 0·0077 | ... |

### TABLE LIV.—*Magnesium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 205 | 1/1000 | 17·7218 | 0·0049 | 0·0070 | ... |
| 206 | 1/100 | 18·4160 | 0·0058 | 0·0083 | ... |
| 207 | 1/10 | 18·5508 | 0·0096 | 0·0137 | ... |
| 208 | N | 17·0679 | 0·0107 | 0·0153 | ... |

## LOW CARBON STEEL. TEMPERATURE OF BOILING WATER.

### TABLE LV.—*Sodium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 377 | 1/1000 | 6·5609 | 0·0063 | 0·0090 | ... |
| 378 | 1/100 | 6·0070 | 0·0061 | 0·0088 | ... |
| 379 | 1/10 | 7·6734 | 0·0066 | 0·0094 | ... |
| 380 | N | 7·1523 | 0·0067 | 0·0096 | ... |

### TABLE LVI.—*Magnesium Sulphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 381 | 1/1000 | 6·3835 | 0·0058 | 0·0083 | ... |
| 382 | 1/100 | 6·7226 | 0·0058 | 0·0083 | ... |
| 383 | 1/10 | 6·8952 | 0·0063 | 0·0090 | ... |
| 384 | N | 7·2419 | 0·0071 | 0·0100 | ... |

### TABLE LVII.—*Sodium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 385 | 1/1000 | 6·3420 | 0·0054 | 0·0077 | ... |
| 386 | 1/100 | 7·4483 | 0·0062 | 0·0089 | ... |
| 387 | 1/10 | 7·2679 | 0·0068 | 0·0097 | ... |
| 388 | N | 6·7082 | 0·0059 | 0·0084 | ... |

### TABLE LVIII.—*Magnesium Chloride.*

| No. | Normality. | Original Weight. | Loss in Weight. | Loss as Ferric Oxide. | Remarks. |
|---|---|---|---|---|---|
| 389 | 1/1000 | 6·7509 | 0·0062 | 0·0089 | ... |
| 390 | 1/100 | 7·1248 | 0·0068 | 0·0097 | ... |
| 391 | 1/10 | 7·5381 | 0·0092 | 0·0131 | ... |
| 392 | N | 7·0032 | 0·0118 | 0·0169 | ... |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### TABLE LIX.—*Sodium Sulphate with N*/1000 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 121 | 1/1000 | 18·2543 | 0·0081 | 155 | Few streaks and spots. |
| 122 | 1/100 | 17·9236 | 0·0052 | 100 | ,, ,, ,, ,, |
| 123 | 1/10 | 18·0497 | 0·0042 | 79 | Several spots. |
| 124 | N | 18·5067 | 0·0057 | 107 | Few spots. |

### TABLE LX.—*Sodium Sulphate with N*/100 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 125 | 1/1000 | 18·2348 | 0·0038 | 71 | No corrosion. Tarnished. |
| 126 | 1/100 | 19·5568 | 0·0049 | 92 | Few spots. |
| 127 | 1/10 | 18·7812 | 0·0060 | 113 | Streaks and spots. |
| 128 | N | 18·0550 | 0·0076 | 143 | ,, ,, ,, |

### TABLE LXI.—*Sodium Sulphate with N*/10 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 129 | 1/1000 | 18·9583 | 0·0036 | 68 | No corrosion. |
| 130 | 1/100 | 18·7540 | 0·0086 | 162 | Well tarnished. |
| 131 | 1/10 | 19·6902 | 0·0158 | 299 | Few rust spots. |
| 132 | N | 18·8220 | 0·0077 | 145 | Few streaks. |

### Table LXII.—*Sodium Sulphate with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 133 | 1/1000 | 18·1663 | 0·0033 | 62 | No corrosion. |
| 134 | 1/100 | 19·1555 | 0·0033 | 62 | ,, ,, |
| 135 | 1/10 | 18·0014 | 0·0120 | 226 | Few spots and streaks. |
| 136 | N | 18·0851 | 0·0124 | 234 | ,, ,, ,, ,, |

## Low Carbon Steel. Temperature of Boiling Water.

### Table LXIII.—*Sodium Sulphate with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 393 | 1/1000 | 7·8221 | 0·0067 | 84 | Few streaks and spots. |
| 394 | 1/100 | 8·7803 | 0·0073 | 91 | ,, ,, ,, ,, |
| 395 | 1/10 | 9·1039 | 0·0095 | 119 | Many minute spots. |
| 396 | N | 8·9027 | 0·0086 | 108 | Few spots and streaks. |

### Table LXIV.—*Sodium Sulphate with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 397 | 1/1000 | 8·2508 | 0·0057 | 71 | Few spots. |
| 398 | 1/100 | 7·5331 | 0·0058 | 73 | ,, ,, |
| 399 | 1/10 | 8·2940 | 0·0098 | 123 | Streaks and spots. |
| 400 | N | 8·7572 | 0·0095 | 119 | ,, ,, ,, |

### Table LXV.—*Sodium Sulphate with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 401 | 1/1000 | 8·9566 | 0·0037 | 46 | No corrosion. |
| 402 | 1/100 | 9·1438 | 0·0091 | 114 | ,, ,, Tarnished. |
| 403 | 1/10 | 9·0236 | 0·0124 | 155 | Few spots and streaks. |
| 404 | N | 9·0028 | 0·0119 | 149 | ,, ,, ,, ,, |

### TABLE LXVI.—*Sodium Sulphate with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 405 | 1/1000 | 9·1142 | 0·0043 | 54 | No corrosion. Tarnished. |
| 406 | 1/100 | 9·2546 | 0·0032 | 40 | ,, ,, ,, |
| 407 | 1/10 | 8·7928 | 0·0114 | 143 | Few rust spots. |
| 408 | N | 8·2371 | 0·0097 | 121 | ,, ,, ,, |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### TABLE LXVII.—*Magnesium Sulphate with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 137 | 1/1000 | 19·1782 | 0·0048 | 91 | Few spots. |
| 138 | 1/100 | 19·2714 | 0·0101 | 191 | Black spots and streaks. |
| 139 | 110 | 18·2537 | 0·0077 | 145 | Black streaks. |
| 140 | N | 18·5238 | 0·0110 | 208 | ,, ,, |

### TABLE LXVIII.—*Magnesium Sulphate with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 141 | 1/1000 | 19·1782 | 0·0046 | 87 | Dull in colour. |
| 142 | 1/100 | 18·7740 | 0·0073 | 138 | Spots over surface. |
| 143 | 1/10 | 18·7936 | 0·0097 | 183 | ,, ,, ,, |
| 144 | N | 18·9597 | 0·0126 | 238 | ,, ,, ,, |

### TABLE LXIX.—*Magnesium Sulphate with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 145 | 1/1000 | 17·1741 | 0·0006 | 11 | Slightly tarnished. |
| 146 | 1/100 | 17·8488 | 0·0013 | 23 | ,, ,, |
| 147 | 1/10 | 18·3274 | 0·0086 | 162 | Few small spots. |
| 148 | N | 18·3712 | 0·0106 | 200 | ,, ,, ,, |

### TABLE LXX.—*Magnesium Sulphate with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 149 | 1/1000 | 18·5256 | 0·0003 | 6 | No corrosion. |
| 150 | 1/100 | 18·1176 | 0·0011 | 21 | Slightly tarnished. |
| 151 | 1/10 | 19·6333 | 0·0065 | 123 | Spots and streaks. |
| 152 | N | 18·8247 | 0·0082 | 151 | ,, ,, ,, |

## LOW CARBON STEEL. TEMPERATURE OF BOILING WATER.

### TABLE LXXI.—*Magnesium Sulphate with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 409 | 1/1000 | 8·3184 | 0·0037 | 46 | Black spots and streaks. |
| 410 | 1/100 | 7·0408 | 0·0160 | 200 | Many spots. |
| 411 | 1/10 | 7·9015 | 0·0097 | 121 | Spots and streaks. |
| 412 | N | 7·1787 | 0·0115 | 144 | ,, ,, ,, |

### TABLE LXXII.—*Magnesium Sulphate with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 413 | 1/1000 | 8·1879 | 0·0042 | 53 | Few black spots. |
| 414 | 1 100 | 9·2314 | 0·0118 | 148 | Many small spots. |
| 415 | 1/10 | 7·9020 | 0·0088 | 110 | Spots over surface. |
| 416 | N | 7·1787 | 0·0108 | 145 | Many small spots. |

### TABLE LXXIII.—*Magnesium Sulphate with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 417 | 1/1000 | 7·8221 | 0·0010 | 13 | Slightly tarnished. |
| 418 | 1/100 | 8·0716 | 0·0013 | 16 | ,, ,, |
| 419 | 1/10 | 8·8831 | 0·0085 | 106 | Few spots over surface. |
| 420 | N | 7·8375 | 0·0100 | 125 | Many small spots. |

### TABLE LXXIV.—*Magnesium Sulphate with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 421 | 1/1000 | 7·2037 | 0·0014 | 18 | Slightly tarnished. |
| 422 | 1/100 | 9·1524 | 0·0009 | 11 | ,, ,, |
| 423 | 1/10 | 8·2165 | 0·0057 | 71 | Few small spots. |
| 424 | N | 8·5532 | 0·0095 | 119 | Spots and streaks. |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### TABLE LXXV.—*Sodium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 153 | 1/1000 | 18·1790 | 0·0075 | 141 | Few black spots. |
| 154 | 1/100 | 18·6186 | 0·0069 | 130 | ,, ,, ,, |
| 155 | 1/10 | 18·2633 | 0·0066 | 124 | ,, ,, ,, |
| 156 | N | 18·9162 | 0·0062 | 117 | ,, ,, ,, |

### TABLE LXXVI.—*Sodium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 157 | 1/1000 | 18·9220 | 0·0120 | 226 | Few black spots. |
| 158 | 1/100 | 18·1262 | 0·0208 | 392 | Spots over surface. |
| 159 | 1/10 | 17·6083 | 0·0267 | 504 | Many small spots. |
| 160 | N | 17·2738 | 0·0210 | 396 | ,, ,, ,, |

### TABLE LXXVII.—*Sodium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 161 | 1/1000 | 18·2339 | 0·0011 | 20 | Tarnished slightly. |
| 162 | 1/100 | 19·3364 | 0·0048 | 91 | Well tarnished. |
| 163 | 1/10 | 18·2891 | 0·0282 | 532 | Many small spots. |
| 164 | N | 18·7213 | 0·0447 | 843 | Covered with rust. |

### TABLE LXXVIII.—*Sodium Chloride with N/*5 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 165 | 1/1000 | 19·2181 | 0·0018 | 34 | Slightly tarnished. |
| 166 | 1/100 | 19·7539 | 0·0078 | 147 | Few spots. |
| 167 | 1/10 | 18·9736 | 0·0262 | 494 | Many small spots. |
| 168 | N | 19·3316 | 0·0453 | 855 | Covered with rust. |

## LOW CARBON STEEL. TEMPERATURE OF BOILING WATER.

### TABLE LXXIX.—*Sodium Chloride with N/*1000 *Potassium Dichromate*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 425 | 1/1000 | 8·6269 | 0·0065 | 81 | Few small spots. |
| 426 | 1/100 | 7·4392 | 0·0095 | 119 | Many small spots. |
| 427 | 1/10 | 7·7890 | 0·0082 | 102 | Several streaks and spots. |
| 428 | N | 7·5234 | 0·0052 | 65 | ,, ,, ,, |

### TABLE LXXX.—*Sodium Chloride with N/*100 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 429 | 1/1000 | 8·8366 | 0·0139 | 174 | Many minute spots. |
| 430 | 1/100 | 7·6972 | 0·0134 | 168 | ,, ,, ,, |
| 431 | 1/10 | 8·1314 | 0·0167 | 209 | Streaks and spots. |
| 432 | N | 8·1278 | 0·0190 | 238 | ,, ,, ,, |

### TABLE LXXXI.—*Sodium Chloride with N/*10 *Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 433 | 1/1000 | 7·6622 | 0·0013 | 16 | Slightly tarnished. |
| 434 | 1/100 | 7·6972 | 0·0052 | 65 | Few spots. |
| 435 | 1/10 | 7·8208 | 0·0254 | 318 | Many minute spots. |
| 436 | N | 8·7049 | 0·0434 | 542 | Badly corroded. |

### TABLE LXXXII.—*Sodium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 437 | 1/1000 | 7·5060 | 0·0014 | 18 | Slightly tarnished. |
| 438 | 1/100 | 7·3744 | 0·0093 | 116 | Few minute spots. |
| 439 | 1/10 | 7·6206 | 0·0254 | 318 | Covered with spots. |
| 440 | N | 7·7049 | 0·0468 | 585 | Badly corroded. |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### TABLE LXXXIII.—*Magnesium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 169 | 1/1000 | 18·6425 | 0·0091 | 172 | Spots and streaks. |
| 170 | 1/100 | 19·0886 | 0·0116 | 219 | Many small spots. |
| 171 | 1/10 | 19·7181 | 0·0132 | 249 | Streaks and spots. |
| 172 | N | 18·0293 | 0·0231 | 436 | ,, ,, ,, |

### TABLE LXXXIV.—*Magnesium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 173 | 1/1000 | 19·1877 | 0·0057 | 108 | Few minute spots. |
| 174 | 1/100 | 18·9242 | 0·0149 | 281 | Many spots. |
| 175 | 1/10 | 18·6621 | 0·0229 | 432 | Badly corroded. |
| 176 | N | 18·4985 | 0·0321 | 606 | ,, ,, |

### TABLE LXXXV.—*Magnesium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 177 | 1/1000 | 17·9358 | 0·0010 | 19 | Tarnished. |
| 178 | 1/100 | 19·4608 | 0·0014 | 26 | Well tarnished. |
| 179 | 1/10 | 18·3315 | 0·0289 | 545 | Many spots and streaks. |
| 180 | N | 18·9670 | 0·0479 | 903 | Badly corroded. |

### TABLE LXXXVI.—*Magnesium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 181 | 1/1000 | 18·4936 | 0·0011 | 20 | Slightly tarnished. |
| 182 | 1/100 | 19·4126 | 0·0011 | 20 | ,, ,, |
| 183 | 1/10 | 18·3315 | 0·0321 | 606 | Many spots and streaks. |
| 184 | N | 19·1092 | 0·0744 | 140 | Badly corroded. |

## LOW CARBON STEEL. TEMPERATURE OF BOILING WATER.

### TABLE LXXXVII.—*Magnesium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 465 | 1/1000 | 7·2108 | 0·0122 | 153 | Many small spots. |
| 466 | 1/100 | 6·9734 | 0·0122 | 153 | Streaks and spots. |
| 467 | 1/10 | 7·0399 | 0·0180 | 225 | ,, ,, ,, |
| 468 | N | 8·0032 | 0·0227 | 284 | Many spots and streaks. |

### TABLE LXXXVIII.—*Magnesium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 469 | 1/1000 | 6·8296 | 0·0045 | 56 | Few spots. |
| 470 | 1/100 | 7·1818 | 0·0163 | 204 | Many minute spots. |
| 471 | 1/10 | 7·1590 | 0·0193 | 241 | Streaks and spots. |
| 472 | N | 7·9684 | 0·0237 | 284 | Covered with rust. |

### TABLE LXXXIX.—*Magnesium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 473 | 1/1000 | 7·3246 | 0·0020 | 25 | Slightly tarnished. |
| 474 | 1/100 | 7·7206 | 0·0015 | 19 | ,, ,, ,, |
| 475 | 1/10 | 8·0416 | 0·0282 | 353 | Covered with spots. |
| 476 | N | 7·3858 | 0·0459 | 574 | Badly corroded. |

TABLE XC.—*Magnesium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 477 | 1/1000 | 7·2677 | 0·0005 | 6 | Slightly tarnished. |
| 478 | 1/100 | 6·7138 | 0·0019 | 24 | Tarnished. |
| 479 | 1/10 | 8·3392 | 0·0419 | 524 | Badly corroded. |
| 480 | N | 7·3858 | 0·0879 | 1099 | ,, ,, |

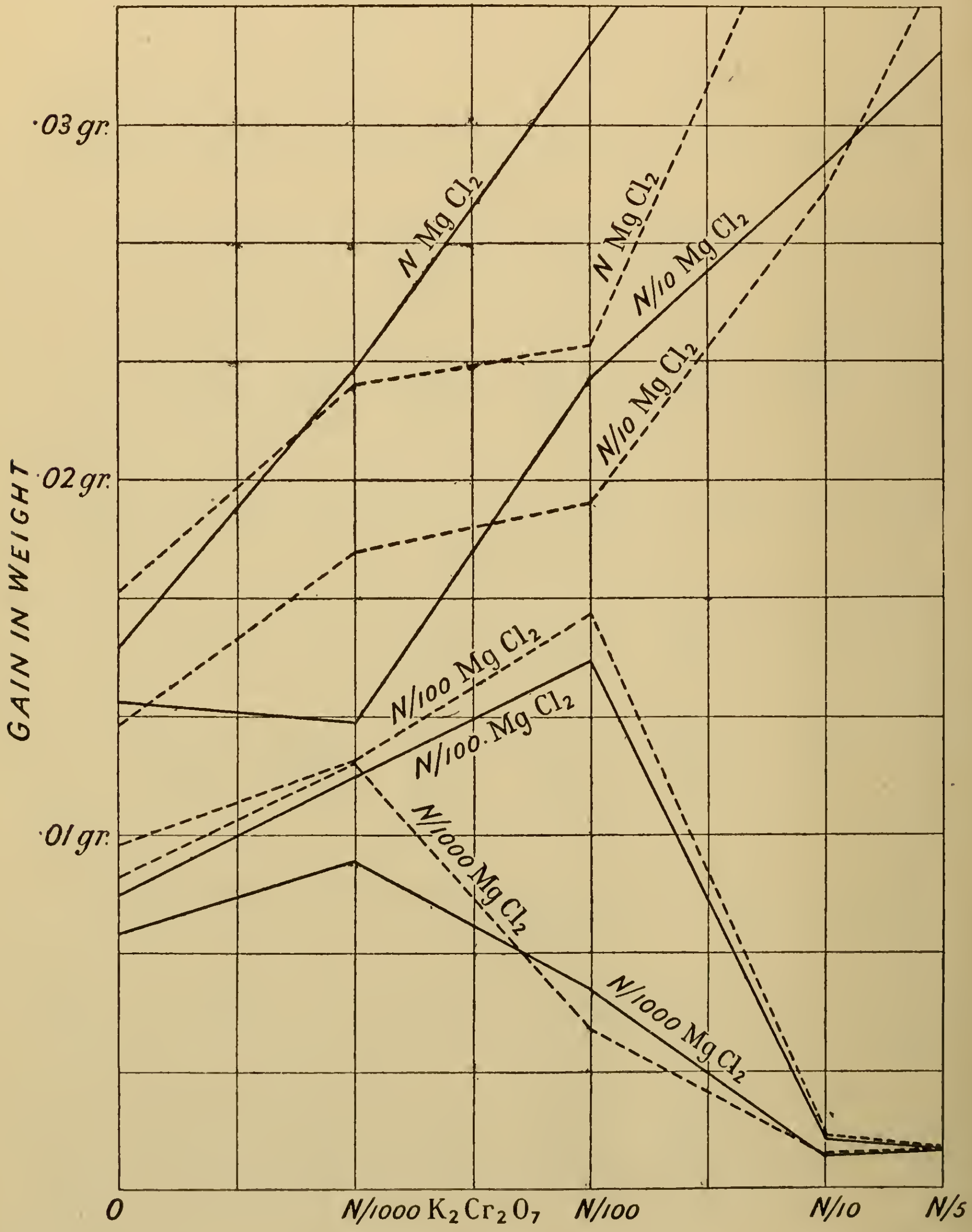

FIG. 10.

## SUMMARY OF RESULTS. (TEMPERATURE OF BOILING WATER.)

### *Solutions of Sodium Sulphate with Potassium Dichromate.*

1. With very dilute solutions of the sulphate the addition of dichromate causes a slight inhibition in corrosion.
2. In the more concentrated solutions the addition of dichromate stimulates corrosion.
3. In many cases the corrosion of the test-plates appeared to be greater in comparison with those in solutions free from dichromate than is actually represented by the gain in weight.
4. Generally the low carbon steel was more easily attacked than the commercially pure iron.

### *Solutions of Magnesium Sulphate with Potassium Dichromate.*

1. With the exception of N/1000 magnesium sulphate the addition of dichromate in small amounts stimulated corrosion.
2. N/10 and N/5 dichromate inhibited corrosion in varying degrees.
3. Generally the low carbon steel was more easily attacked than the commercially pure iron.
4. The action of the magnesium sulphate solutions were less than those of sodium sulphate.

### *Solutions of Sodium Chloride with Potassium Dichromate.*

1. N/1000 dichromate had practically no effect upon the corrosion of the plates, although there was a general tendency towards inhibition.
2. N/100 dichromate stimulated corrosion in every case.
3. With the more dilute solutions of sodium chloride, N/10 and N/5 dichromate inhibited corrosion.
4. N/10 and N/5 dichromate in the more concentrated solutions of sodium chloride stimulated corrosion to a marked extent.
5. Commercially pure iron showed a slightly greater increase in the rate of corrosion than did the low carbon steel.
6. Sodium chloride and potassium dichromate interacted with water to produce traces of hydrochloric acid.

### *Solutions of Magnesium Chloride with Potassium Dichromate.*

1. In all cases the action of these solutions upon the iron and steel was greater than the corresponding solutions of sodium chloride.
2. N/10 and N/5 dichromate in the dilute solutions of magnesium chloride inhibited corrosion.
3. In all other solutions increase in either the dichromate or the chloride produced conditions that strongly stimulated corrosion.
4. Magnesium chloride and potassium dichromate seemed to interact with water to produce hydrochloric acid.

## Action of Di-sodium Phosphate in the Presence of Sodium Sulphate and Sodium Chloride.

When an iron strip is made the anode in an electric circuit and placed in a solution of di-sodium phosphate, it is passivified. It has been shown by Heyn and Bauer that iron placed in this solution will not corrode as readily as in solutions of commoner salts, and that a point or "limiting concentration" is reached where all corrosive action ceases. As this phosphate is used to a certain extent as a boiler water softener, it was decided to study its effect in solutions of sodium chloride and sodium sulphate upon the iron and steel used in other experiments. The tests were conducted in the same manner as previously described and the data obtained follows.

The graphic representation of the results of the corrosion tests for the low carbon steel is shown by dotted lines, while that of the commercially pure iron is indicated by continuous lines.

Commercially Pure Iron. Room Temperature.

Table XCI.—*Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 241 | 1/1000 | 18·7146 | 0·1494 | 75 | Badly corroded. |
| 242 | 1/100 | 17·1147 | 0·0190 | 9 | Green and brown rust. |
| 243 | 1/10 | 18·4924 | 0·0005[1] | 0 | No corrosion. |
| 244 | N | 18·0340 | 0·0001[1] | 0 | ,, ,, |

[1] Gain in weight.

## LOW CARBON STEEL. ROOM TEMPERATURE.

### TABLE XCII.—*Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 369 | 1/1000 | 6·4191 | 0·1339 | 61 | Badly corroded. |
| 370 | 1/100 | 6·9566 | 0·0232 | 10 | Greenish brown rust. |
| 371 | 1/10 | 7·3431 | 0·0004[1] | 0 | No corrosion. |
| 372 | N | 6·8778 | 0·0000 | 0 | ,, ,, |

## COMMERCIALLY PURE IRON. ROOM TEMPERATURE.

### TABLE XCIII.—*Sodium Sulphate with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 89 | 1/1000 | 17·6301 | 0·1893 | 95 | Badly corroded. |
| 90 | 1/100 | 17·3585 | 0·1792 | 85 | ,, ,, |
| 91 | 1/10 | 18·3143 | 0·1850 | 93 | ,, ,, |
| 92 | N | 18·9224 | 0·1109 | 55 | ,, ,, |

### TABLE XCIV.—*Sodium Sulphate with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 93 | 1/1000 | 18·7378 | 0·0489 | 24 | Covered with a light brown layer mottled with greenish streaks. |
| 94 | 1/100 | 19·5230 | 0·0505 | 25 | |
| | 1/10 | 19·6386 | 0·0613 | 31 | |
| | N | 19·3583 | 0·0861 | 33 | Badly corroded. |

### TABLE XCV.—*Sodium Sulphate with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 97 | 1/1000 | 19·2083 | 0·0002[1] | 0 | No corrosion. |
| 98 | 1/100 | 18·5526 | 0·0061 | 3 | Small lumpy green spots. |
| 99 | 1/10 | 18·9841 | 0·0195 | 10 | Large ,, ,, ,, |
| 100 | N | 19·6082 | 0·0309 | 15 | Covered with brown rust. |

---

[1] Gain in weight.

### Table XCVI.—*Sodium Sulphate with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 101 | 1/1000 | 20·0196 | 0·0004[1] | 0 | No corrosion. |
| 102 | 1/100 | 19·3779 | 0·0000 | 0 | ,, ,, |
| 103 | 1/10 | 19·9065 | 0·0032 | 1 | Small green festoons on edge. |
| 104 | N | 18·7244 | 0·0266 | 13 | Greenish-brown deposits. |

## Low Carbon Steel. Room Temperature.

### Table XCVII.—*Sodium Sulphate with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 209 | 1/1000 | 7·2392 | 0·2221 | 111 | Badly corroded. |
| 210 | 1/100 | 6·7040 | 0·1597 | 80 | ,, ,, |
| 211 | 110 | 7·7197 | 0·1862 | 93 | ,, ,, |
| 212 | N | 7·2695 | 0·1428 | 71 | ,, ,, |

### Table XCVIII.—*Sodium Sulphate with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 213 | 1/1000 | 7·0472 | 0·0285 | 14 | Few small spots. |
| 214 | 1/100 | 7·7363 | 0·0304 | 15 | Brown spots and streaks. |
| 215 | 1/10 | 7·5623 | 0·0733 | 36 | Badly corroded. |
| 216 | N | 7·0303 | 0·0842 | 42 | ,, ,, |

### Table XCIX.—*Sodium Sulphate with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 217 | 1/1000 | 7·7705 | 0·0003[1] | 0 | No corrosion. |
| 218 | 1/100 | 7·3620 | 0·0182 | 9 | Few minute green spots. |
| 219 | 1/10 | 6·6200 | 0·0183 | 9 | ,, ,, ,, ,, |
| 220 | N | 7·7727 | 0·0427 | 21 | Well corroded. |

[1] Gain in weight.

TABLE C.—*Sodium Sulphate with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 221 | 1/1000 | 7·3201 | 0·0001[1] | 0 | No corrosion. |
| 222 | 1/100 | 7·6792 | 0·0002[1] | 0 | ,, ,, |
| 223 | 1/10 | 7·5185 | 0·0093 | 5 | Few minute green spots |
| 224 | N | 6·9973 | 0·0399 | 20 | Few large ,, ,, |

[1] Gain in weight.

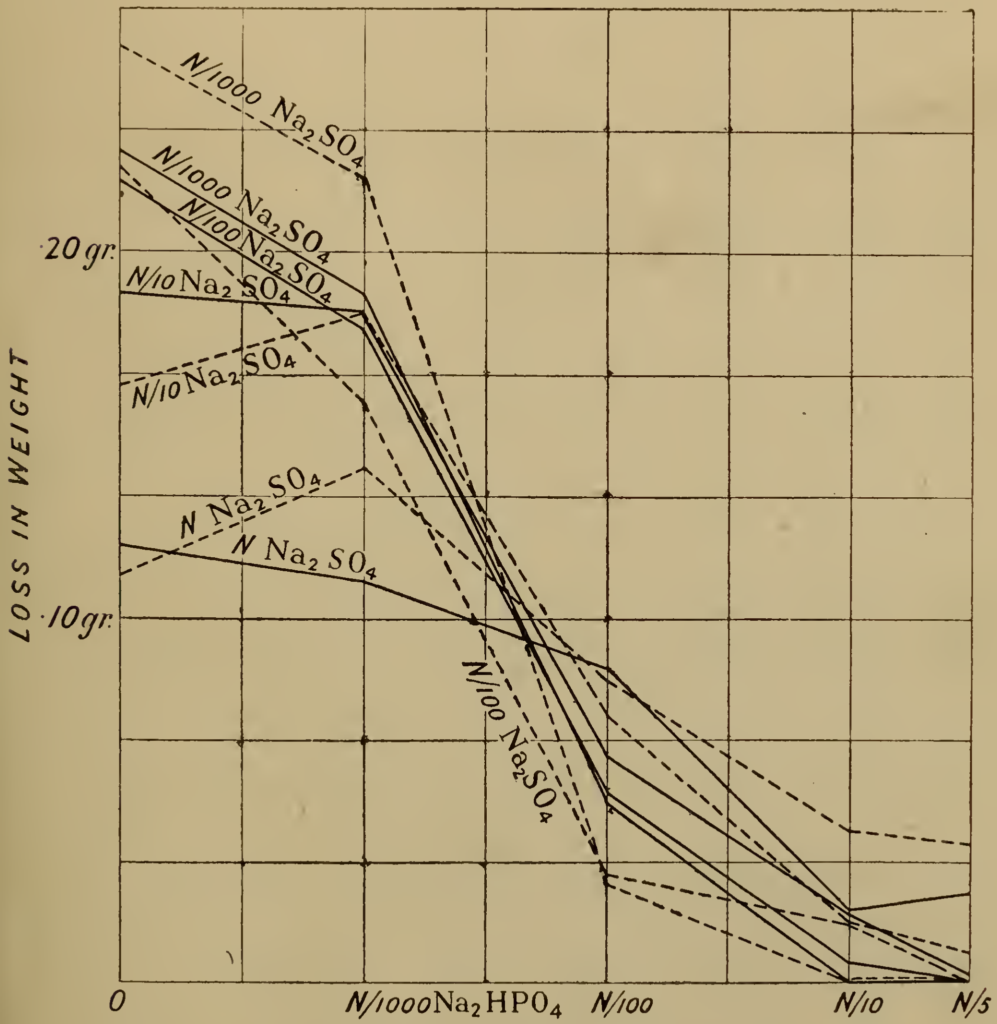

FIG. 11.—Graph showing the Behaviour of Low Carbon Steel and Commercially Pure Iron in Solutions of Sodium Sulphate and Di-sodium Phosphate. (Room Temperature.)

## COMMERCIALLY PURE IRON. ROOM TEMPERATURE.

### TABLE CI.—*Sodium Chloride with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 105 | 1/1000 | 18·1240 | 0·1424 | 71 | Badly corroded. |
| 106 | 1/100 | 18·9518 | 0·1376 | 69 | ,, ,, |
| 107 | 1/10 | 19·0994 | 0·1260 | 63 | ,, ,, |
| 108 | N | 18·0001 | 0·1336 | 67 | ,, ,, |

### TABLE CII.—*Sodium Chloride with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 109 | 1/1000 | 18·2028 | 0·0917 | 46 | Badly corroded. |
| 110 | 1/100 | 19·1043 | 0·0962 | 48 | ,, ,, |
| 111 | 1/10 | 18·7914 | 0·0208 | 10 | Green streaks. |
| 112 | N | 18·9768 | 0·0138 | 6 | ,, ,, |

### TABLE CIII.—*Sodium Chloride with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 113 | 1/1000 | 18·8776 | 0·0003[1] | 0 | No corrosion. |
| 114 | 1/100 | 18·9418 | 0·0063 | 3 | Few green spots. |
| 115 | 1/10 | 17·2943 | 0·0350 | 17 | Large green spots. |
| 116 | N | 19·1335 | 0·0243 | 12 | ,, ,, ,, |

### TABLE CIV.—*Sodium Chloride with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 117 | 1/1000 | 17·3865 | 0·0009[1] | 0 | No corrosion. |
| 118 | 1/100 | 18·1178 | 0·0009[1] | 0 | ,, ,, |
| 119 | 1/10 | 20·0233 | 0·0316 | 15 | Green spots and streaks. |
| 120 | N | 18·3372 | 0·0339 | 17 | ,, ,, ,, ,, |

---

[1] Gain in weight.

### LOW CARBON STEEL. ROOM TEMPERATURE.

TABLE CV.—*Sodium Chloride with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 225 | 1/1000 | 6·6189 | 0·1643 | 76 | Badly corroded. |
| 226 | 1/100 | 6·6663 | 0·1682 | 77 | ,, ,, |
| 227 | 1/10 | 6·5467 | 0·1497 | 69 | ,, ,, |
| 228 | N | 7·4723 | 0·1477 | 68 | ,, ,, |

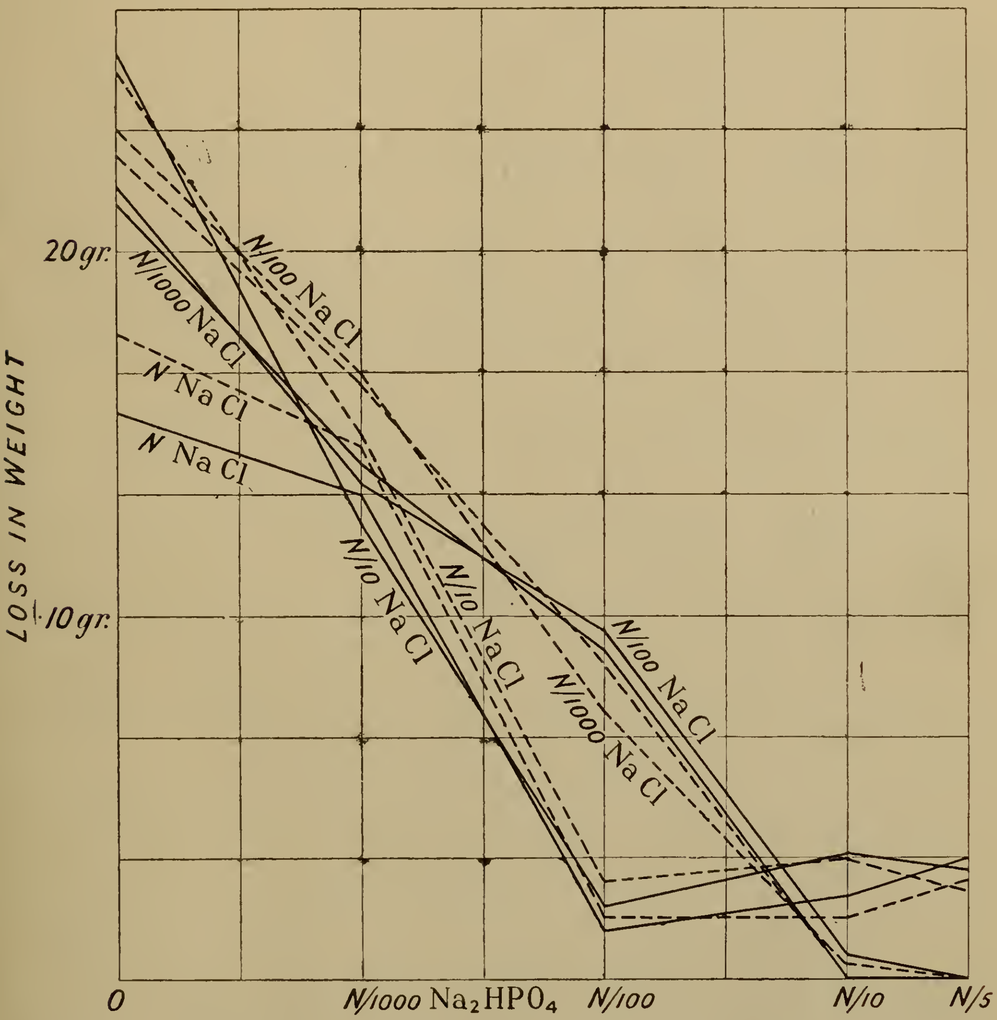

FIG. 12.—Graph showing the Behaviour of Low Carbon Steel and Commercially Pure Iron in Solutions of Sodium Chloride and Di-sodium Phosphate. (Room Temperature.)

### Table CVI.—*Sodium Chloride with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 229 | 1/1000 | 6·7869 | 0·0877 | 40 | Badly corroded. |
| 230 | 1/100 | 7·6427 | 0·0724 | 29 | ,, ,, |
| 231 | 1/10 | 7·0475 | 0·0273 | 13 | Green streaks and spots. |
| 232 | N | 6·8192 | 0·0159 | 7 | ,, ,, ,, ,, |

### Table CVII.—*Sodium Chloride with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 233 | 1/1000 | 7·3540 | 0·0004[1] | 0 | No corrosion. |
| 234 | 1/100 | 6·5625 | 0·0048 | 2 | Few minute green spots. |
| 235 | 1/10 | 7·0781 | 0·0344 | 15 | Green streaks and spots. |
| 236 | N | 7·5965 | 0·0169 | 8 | ,, ,, ,, ,, |

### Table CVIII.—*Sodium Chloride with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 237 | 1/1000 | 6·3236 | 0·0001[1] | 0 | No corrosion. |
| 238 | 1/100 | 6·1297 | 0·0011[1] | 0 | ,, ,, |
| 239 | 1/10 | 6·6065 | 0·0250 | 11 | Green streaks and spots. |
| 240 | N | 7·5117 | 0·0271 | 13 | ,, ,, ,, ,, |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### Table CIX.—*Di-sodium Phosphate*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 245 | 1/1000 | 17·4359 | 0·0143 | 269 | Greenish brown streaks. |
| 246 | 1/100 | 17·9364 | 0·0102 | 194 | ,, ,, ,, |
| 247 | 1/10 | 16·8934 | 0·0058 | 108 | Green spots. |
| 248 | N | 17·0009 | 0·0024 | 46 | Tarnished. |

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[1] Gain in weight.

## Low Carbon Steel. Temperature of Boiling Water.

### Table CX.—*Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 373 | 1/1000 | 6·5418 | 0·0125 | 156 | Green and brown spots. |
| 374 | 1/100 | 7·0031 | 0·0110 | 138 | ,, ,, ,, ,, |
| 375 | 1/10 | 6·8985 | 0·0054 | 68 | Small green spots. |
| 376 | N | 6·5718 | 0·0019 | 24 | Well tarnished. |

## Commercially Pure Iron. Boiling Temperature.

### Table CXI.—*Sodium Sulphate with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 333 | 1/1000 | 19·2281 | 0·0170 | 321 | Spots over surface. |
| 334 | 1/100 | 19·4353 | 0·0142 | 268 | Green spots. |
| 335 | 1/10 | 18·1332 | 0·0125 | 236 | Well tarnished. |
| 336 | N | 19·3526 | 0·0104 | 196 | ,, ,, |

### Table CXII.—*Sodium Sulphate with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 337 | 1/1000 | 19·1982 | 0·0156 | 294 | Green streaks. |
| 338 | 1/100 | 18·3059 | 0·0140 | 264 | ,, ,, |
| 339 | 1/10 | 18·9705 | 0·0155 | 293 | Green spots. |
| 340 | N | 18·7855 | 0·0137 | 268 | Whole plate dull green. |

### Table CXIII.—*Sodium Sulphate with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 341 | 1/1000 | 19·6320 | 0·0146 | 275 | Well tarnished. |
| 342 | 1/100 | 19·7485 | 0·0196 | 370 | Green spots and streaks. |
| 343 | 1/10 | 19·5355 | 0·0169 | 319 | Badly tarnished. Several green spots. |
| 344 | N | 19·2326 | 0·0117 | 221 | Green streaks. |

### TABLE CXIV.—*Sodium Sulphate with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 345 | 1/1000 | 18·4341 | 0·0045 | 85 | Tarnished. |
| 346 | 1/100 | 19·6283 | 0·0143 | 270 | Green spots. |
| 347 | 1/10 | 18·1374 | 0·0121 | 228 | Badly tarnished. |
| 348 | N | 19·0593 | 0·0117 | 221 | Green streaks and spots. |

## LOW CARBON STEEL. BOILING TEMPERATURE.

### TABLE CXV.—*Sodium Sulphate with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 449 | 1/1000 | 7·3269 | 0·0174 | 218 | Green spots and streaks. |
| 450 | 1/100 | 7·6484 | 0·0202 | 252 | Faint green streaks. |
| 451 | 1/10 | 8·0451 | 0·0132 | 165 | Dull colour. |
| 452 | N | 7·4946 | 0·0134 | 168 | Tarnished. |

### TABLE CXVI.—*Sodium Sulphate with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 453 | 1/1000 | 7·7013 | 0·0181 | 226 | Green spots and streaks. |
| 454 | 1/100 | 7·5766 | 0·0200 | 250 | ,, ,, ,, ,, |
| 455 | 1/10 | 8·0451 | 0·0188 | 225 | Green streaks. |
| 456 | N | 7·4946 | 0·0134 | 193 | Many small green spots. |

### TABLE CXVII.—*Sodium Sulphate with N/10 Sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 457 | 1/1000 | 7·0807 | 0·0174 | 217 | Many green spots. |
| 458 | 1/100 | 7·4831 | 0·0176 | 220 | ,, ,, ,, |
| 459 | 1/10 | 7·7700 | 0·0191 | 239 | ,, ,, ,, |
| 460 | N | 7·9405 | 0·0142 | 178 | ,, ,, ,, |

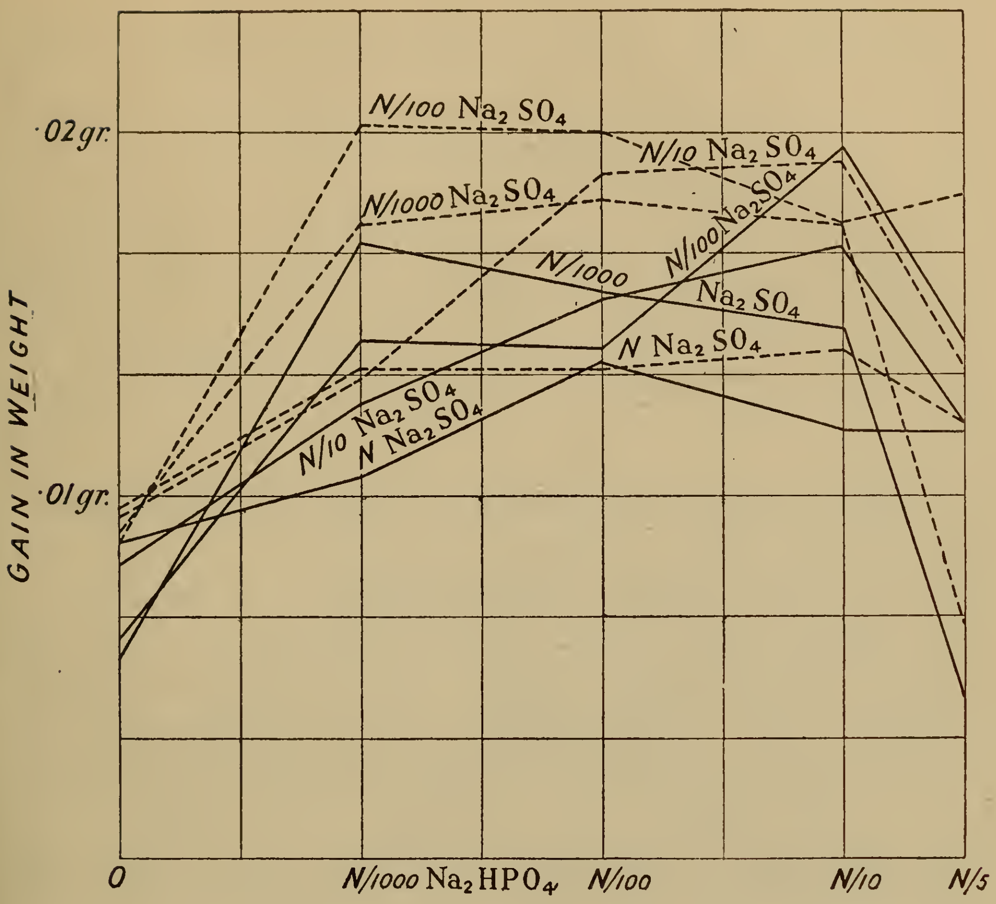

Fig. 13.—Graph showing the Action of Solutions of Sodium Sulphate and Di-sodium Phosphate upon Low Carbon Steel and Commercially Pure Iron. (Temperature of Boiling Water.)

Table CXVIII.—*Sodium Sulphate with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 461 | 1/1000 | 7·0911 | 0·0067 | 84 | Tarnished. Small spots. |
| 462 | 1/100 | 7·6702 | 0·0182 | 228 | ,, Large ,, |
| 463 | 1/10 | 7·9916 | 0·0136 | 170 | Large green spots. |
| 464 | N | 7·8441 | 0·0122 | 153 | ,, ,, ,, |

## COMMERCIALLY PURE IRON. TEMPERATURE OF BOILING WATER.

### TABLE CXIX.—*Sodium Chloride with N/1000 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 349 | 1/1000 | 19·0371 | 0·0136 | 257 | Many green lumpy spots. |
| 350 | 1/100 | 18·8365 | 0·0139 | 262 | ,, ,, ,, ,, |
| 351 | 1/10 | 16·4222 | 0·0098 | 185 | Greenish coating. |
| 352 | N | 18·5260 | 0·0063 | 118 | Well tarnished. |

### TABLE CXX.—*Sodium Chloride with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 353 | 1/1000 | 18·9083 | 0·0096 | 181 | Green streaks and spots. |
| 354 | 1/100 | 17·0315 | 0·0130 | 245 | ,, ,, ,, ,, |
| 355 | 1/10 | 18·1345 | 0·0100 | 190 | Small green spots. |
| 356 | N | 17·5985 | 0·0115 | 216 | Green coating. |

### TABLE CXXI.—*Sodium Chloride with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 357 | 1/1000 | 18·1934 | 0·0068 | 128 | Few green spots and lumps. |
| 358 | 1/100 | 17·6379 | 0·0110 | 207 | Green spots and streaks. |
| 359 | 1/10 | 18·3824 | 0·0169 | 318 | Green lumps. |
| 360 | N | 18·2926 | 0·0159 | 300 | Green coating and lumps. |

### TABLE CXXII.—*Sodium Chloride with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 361 | 1/1000 | 18·4672 | 0·0020 | 38 | Well tarnished. |
| 362 | 1/100 | 18·1511 | 0·0044 | 83 | Minute green spots. |
| 363 | 1/10 | 18·1273 | 0·0135 | 257 | Few green lumps. |
| 364 | N | 18·2734 | 0·0151 | 288 | Green lumps. |

### LOW CARBON STEEL. TEMPERATURE OF BOILING WATER.

### TABLE CXXIII.—*Sodium Chloride with N/1000 Di-sodium Phosphate.*

| N . | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 481 | 1/1000 | 6·7084 | 0·0169 | 210 | Green coating with spots. |
| 482 | 1/100 | 6·7072 | 0·0153 | 191 | ,, ,, ,, ,, |
| 483 | 1/10 | 8·0876 | 0·0123 | 154 | Green spots and streaks. |
| 484 | N | 8·2663 | 0·0071 | 89 | Green coating. Tarnished. |

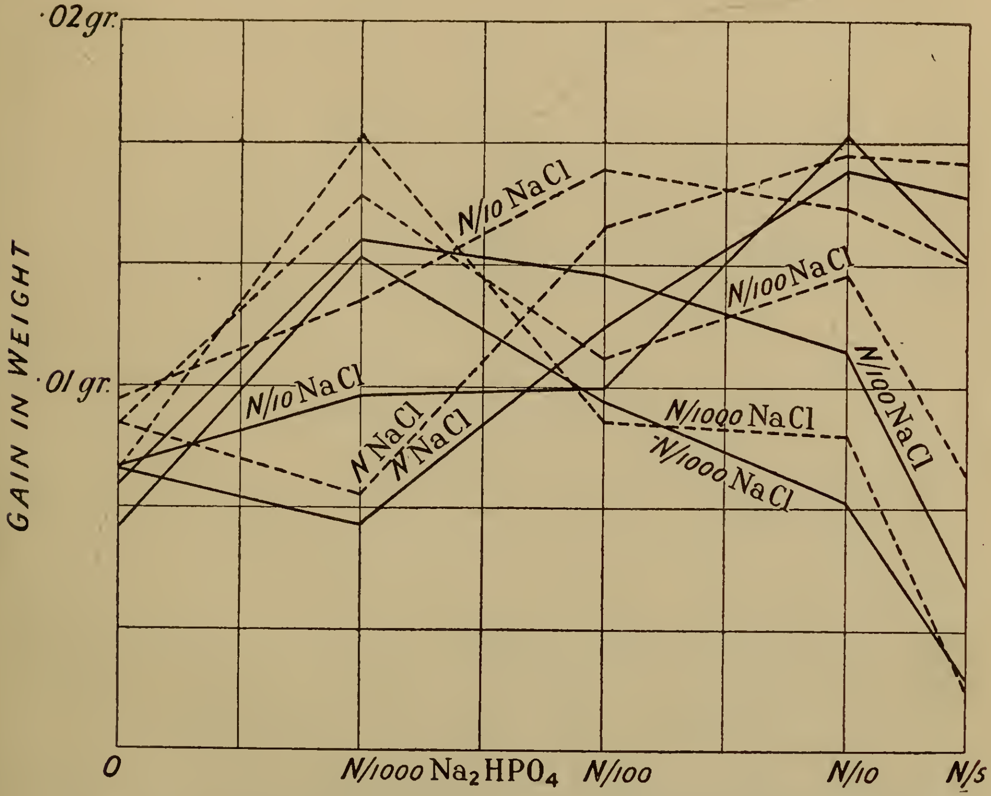

FIG. 14.—Graph showing the Action of Low Carbon Steel and Commercially Pure Iron in Solutions of Sodium Chloride and Di-sodium Phosphate. (Temperature of Boiling Water.)

### TABLE CXXIV.—*Sodium Chloride with N/100 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 529 | 1/1000 | 6·2168 | 0·0091 | 114 | Dark green coating. |
| 530 | 1/100 | 6·9987 | 0·0107 | 134 | Green coating and spots. |
| 531 | 1/10 | 8·1169 | 0·0159 | 199 | ,, ,, ,, ,, |
| 532 | N | 8·2188 | 0·0147 | 184 | Green-brown coating. |

TABLE CXXV.—*Sodium Chloride with N/10 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 533 | 1/1000 | 7·1474 | 0·0087 | 109 | Tarnished. Green colour. |
| 534 | 1/100 | 6·7447 | 0·0131 | 164 | Spots. |
| 535 | 1/10 | 6·8138 | 0·0149 | 186 | Green coating and spots. |
| 536 | N | 7·4259 | 0·0164 | 205 | ,, ,, ,, ,, |

TABLE CXXVI.—*Sodium Chloride with N/5 Di-sodium Phosphate.*

| No. | Normality. | Original Weight. | Gain in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 537 | 1/1000 | 7·5677 | 0·0016 | 20 | Well tarnished. |
| 538 | 1/100 | 6·6022 | 0·0073 | 91 | Few green spots. |
| 539 | 1/10 | 7·9037 | 0·0135 | 169 | Green lumpy spots. |
| 540 | N | 7·0790 | 0·0162 | 203 | ,, ,, ,, |

## SUMMARY OF RESULTS.

### *Room Temperature.*

*Sodium Sulphate.*—In all cases di-sodium phosphate inhibits corrosion, but not to the extent manifested by potassium dichromate.

With N/1000 di-sodium phosphate, the rate of corrosion is only slightly reduced, but in solutions containing greater amounts of this salt, the degree of inhibition is much more marked.

The concentration of the sodium sulphate remaining constant, an increase in the amount of phosphate produces a decrease in the rate of corrosion. However, if the sulphate varies and the concentration of the phosphate remains constant, an increase in corrosive action follows.

With solutions containing N/100 or more of phosphate, the action of the electrolytes upon the iron is shown by the formation of dark green or greenish brown spots and streaks.

There is a noticeable difference in the behaviour of the two different types of test-plates.

When corrosion did not take place, the test-plates were found to be in the active condition, as they were readily attacked by 1·20 nitric acid.

*Sodium Chloride.*—The above summary describing the action of sodium sulphate and di-sodium phosphate also applies in a general way to conditions produced by solutions of sodium chloride and the phosphate. However, with the normal solutions an increase of phosphate from N/10 to N/5 will give a slight increase in the rate of corrosion. Further, if the phosphate is kept constant and the amount of sodium chloride is varied a decrease in corrosion sometimes results, especially with N/100 phosphate.

### *Temperature of Boiling Water.*

It was found that if di-sodium phosphate be introduced into solutions of sodium chloride or sodium sulphate, an increase in the rate of corrosion of the test-plates was obtained.

In N/5 di-sodium phosphate there is a general tendency for the rate of corrosion to decrease.

The low carbon steel showed a higher rate of corrosion than did the commercially pure iron.

## ACTION OF POTASSIUM DICHROMATE ON GALVANISED IRON IN THE PRESENCE OF SODIUM CHLORIDE AND SODIUM SULPHATE.

The use of zinc was suggested some years ago as a means for preventing corrosion in boilers. Slabs of zinc were placed in the boiler in contact with the iron or steel, which was preserved at the expense of the zinc. This method for preventing corrosion was adopted on board ships and made particular use of by tramp steamers, the results being highly satisfactory. However, the great objection to the method is the rapid manner in which the zinc will go into solution under boiler conditions. As Dunstan and Hill[1] have shown that zinc can be passivified by means of potassium dichromate, and in view of the fact that this salt will greatly reduce the rate of corrosion of iron and steel in the presence of large amounts of common boiler salts at room temperature, as shown in previous experiments, it was thought that possibly the rate of solution of the zinc would be likewise reduced in the presence of potassium dichromate without hindering its action toward the iron. Accordingly solutions of varying concentrations of sodium chloride and sodium sulphate containing potassium dichromate in different amounts were made up, and test-plates of galvanised iron, similar in size to those previously used, were introduced into the solutions. Tests were run both at room temperature and at the temperature of boiling water for two weeks. The conditions under which the tests were performed were the same as given on p. 240.

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[1] *Transactions of the Chemical Socicty*, 1911, vol. 99, p. 1861.

In cleaning the plates after they had stood in the solutions great difficulty was experienced. After trying several means for cleaning them, it was decided to simply wash them thoroughly with water and then with alcohol and dry. It was found to be almost impossible to secure very good checks on the tests. This is attributed to improper means for cleaning, formation of zinc chromate, and to the great variation in the size of the crystals of zinc on the galvanised iron. The rate of solution of the plates in water was taken as a standard.

Tests were run with solutions containing varying amounts of potassium dichromate. The plates, after standing for a brief period, especially in the stronger solutions, became very bright ; but at the end of the two weeks it was observed that much more zinc had gone into solution than when the plates were immersed only in water. This is easily explained by the fact that the addition of the potassium dichromate would increase the conductivity of the solutions and thus cause an increase in galvanic action.

A glance at the following results will show that the presence of potassium dichromate in either solutions of sodium chloride or sodium sulphate will stimulate the solution of the zinc rather than inhibit it. If the amount of potassium dichromate is kept constant and the concentration of the sodium chloride or sodium sulphate is increased, the rate of the destruction of the zinc is increased. On the other hand, if the concentration of the potassium dichromate is varied and that of the sodium chloride or sodium sulphate kept constant, the rate at which the zinc is attacked is far more vigorous.

The action of solutions of sodium sulphate and potassium dichromate is illustrated in Fig. 15 by the dotted lines, while the continuous lines show the behaviour of the galvanised iron in solutions of sodium chloride and potassium dichromate. The

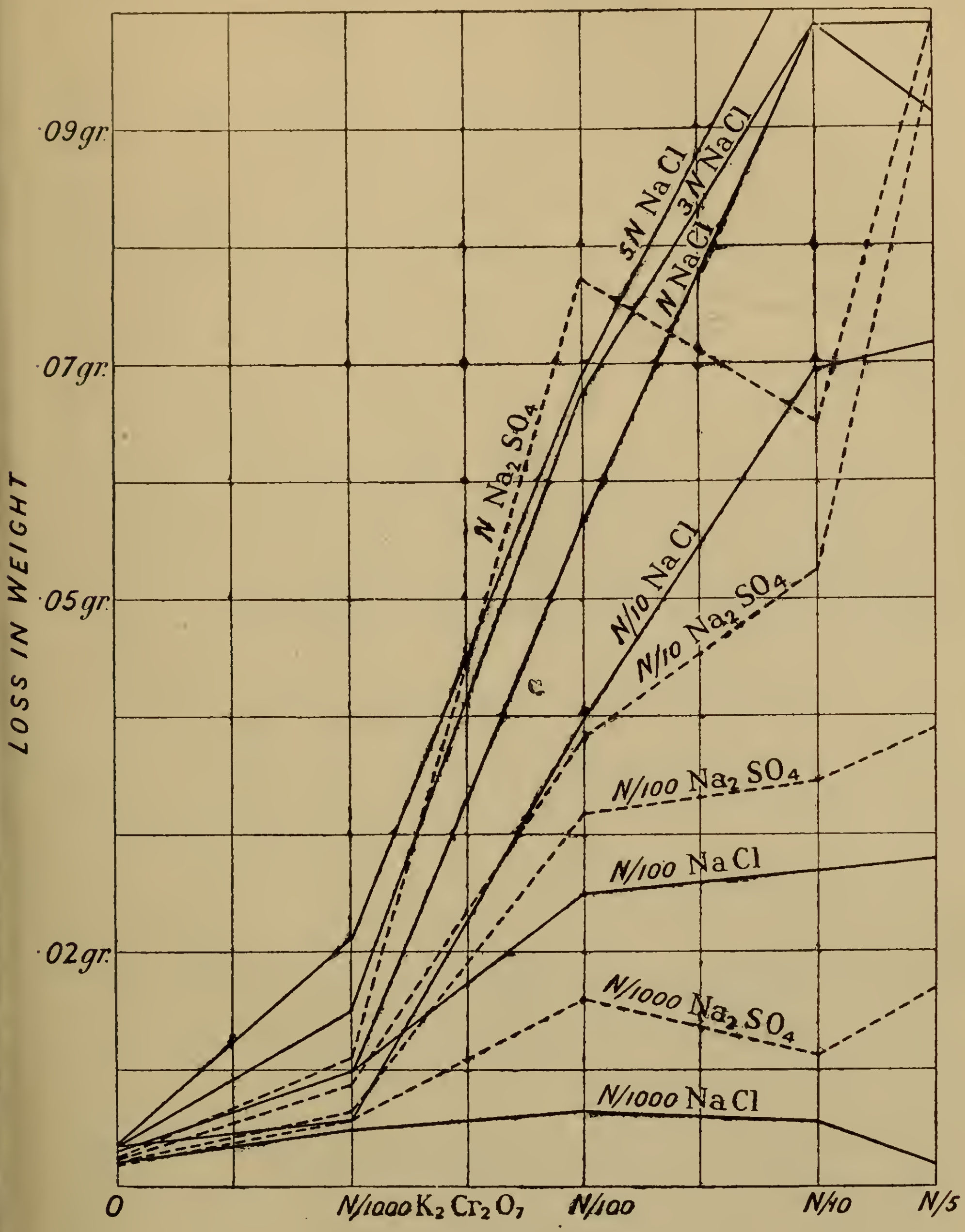

Fig. 15.

great increase in the rate of corrosion of the zinc upon the addition of the various substances to the solutions is due to a corresponding acceleration of galvanic action between the zinc and the iron.

The plates immersed in the more concentrated solutions of potassium dichromate and sodium sulphate or sodium chloride were all of a yellow colour, the intensity of which depended upon the strength of the solutions. After these plates had been thoroughly washed with water, they were treated with hydrochloric acid to dissolve the zinc together with the yellow coating. The resulting solutions were tested for chromium. In every case this element was identified, much more chromium being found in the solutions obtained from the plates having the deep yellow colour than those possessing a lighter colour. Thus the yellow deposit on the galvanised iron was due to the formation of zinc chromate.

With the tests run at the temperature of boiling water no quantitative results were obtained. In every case the plates were badly attacked, and in some instances flakes of metallic zinc had fallen from the plates. In many others all the zinc had dissolved and the solutions had attacked the iron. This was especially true of the sodium chloride solutions.

### GALVANISED IRON. ROOM TEMPERATURE.

TABLE CXXVII.—*Action of Water.*

| No. | Original Weight. | Loss in Weight. | Remarks. |
|---|---|---|---|
| A | 5·9566 | 0·0023 | No visible action. |
| B | 6·1762 | 0·0029 | ,, ,, ,, |
| C | 6·2771 | 0·0038 | ,, ,, ,, |
| D | 5·9928 | 0·0032 | ,, ,, ,, |
| E | 6·0821 | 0·0026 | ,, ,, ,, |

TABLE CXXVIII.—*Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 525 | 1/1000 | 5·8927 | 0·0039 | 130 | No visible action. |
| 526 | 1/100 | 6·1605 | 0·0021 | 70 | Metal brighter. |
| 527 | 1/10 | 6·3310 | 0·0064 | 213 | Metal bright. |
| 528 | 1/5 | 6·4807 | 0·0065 | 216 | ,, ,, |

## GALVANISED IRON. ROOM TEMPERATURE.

### TABLE CXXIX.—*Sodium Sulphate with N/1000 Potassium Dichromate*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 485 | 1/1000 | 5·7442 | 0·0059 | 197 | No visible change. |
| 486 | 1/100 | 5·4649 | 0·0064 | 213 | ,, ,, ,, |
| 487 | 1/10 | 5·7579 | 0·0088 | 293 | ,, ,, ,, |
| 488 | N | 6·1893 | 0·0114 | 380 | ,, ,, ,, |

### TABLE CXXX.—*Sodium Sulphate with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 489 | 1/1000 | 5·5231 | 0·0159 | 530 | No visible change. |
| 490 | 1/100 | 5·8883 | 0·0320 | 1063 | ,, ,, ,, |
| 491 | 1/10 | 5·5643 | 0·0383 | 1277 | Light yellow in colour. |
| 492 | N | 5·7842 | 0·0775 | 2583 | ,, ,, ,, ,, |

### TABLE CXXXI.—*Sodium Sulphate with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 493 | 1/1000 | 5·7247 | 0·0114 | 380 | No visible change. |
| 494 | 1/100 | 5·5725 | 0·0345 | 1150 | Light yellow. |
| 495 | 1/10 | 5·7728 | 0·0528 | 1760 | Deep yellow. |
| 496 | N | 5·4051 | 0·0649 | 2163 | ,, ,, |

### TABLE CXXXII.—*Sodium Sulphate with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 497 | 1/1000 | 6·0362 | 0·0171 | 570 | No visible change. |
| 498 | 1/100 | 5·2548 | 0·0389 | 1297 | Deep yellow. |
| 499 | 1/10 | 6·0078 | 0·0950 | 3167 | ,, ,, |
| 500 | N | 5·7815 | 0·0986 | 3287 | ,, ,, |

## Galvanised Iron. Room Temperature.

Table CXXXIII.—*Sodium Chloride with N/1000 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 501 | 1/1000 | 5·8586 | 0·0052 | 173 | No visible change. |
| 502 | 1/100 | 5·8087 | 0·0097 | 323 | ,, ,, ,, |
| 503 | 1/10 | 5·3215 | 0·0061 | 203 | ,, ,, ,, |
| 504 | N | 5·1719 | 0·0097 | 323 | ,, ,, ,, |
| 505 | 3 N | 5·5820 | 0·0145 | 483 | ,, ,, ,, |
| 506 | 5 N | 6·1767 | 0·0210 | 700 | ,, ,, ,, |

Table CXXXIV.—*Sodium Chloride with N/100 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 507 | 1/1000 | 5·9378 | 0·0062 | 207 | No visible change. |
| 508 | 1/100 | 6·0623 | 0·0248 | 827 | ,, ,, ,, |
| 509 | 1/10 | 6·1338 | 0·0398 | 1327 | ,, ,, ,, |
| 510 | N | 6·3237 | 0·0568 | 1893 | ,, ,, ,, |
| 511 | 3 N | 6·0456 | 0·0675 | 2250 | Light yellow in colour. |
| 512 | 5 N | 6·0240 | 0·0691 | 2333 | ,, ,, ,, ,, |

Table CXXXV.—*Sodium Chloride with N/10 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight. | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 513 | 1/1000 | 6·3159 | 0·0055 | 183 | No visible change. |
| 514 | 1/100 | 5·8117 | 0·0270 | 900 | ,, ,, ,, |
| 515 | 1/10 | 5·8750 | 0·0694 | 2313 | Light yellow in colour. |
| 516 | N | 6·1337 | 0·0987 | 3290 | Deep yellow. |
| 517 | 3 N | 6·0204 | 0·0981 | 3270 | ,, ,, |
| 518 | 5 N | 5·9321 | 0·1130 | 3767 | ,, ,, |

Table CXXXVI.—*Sodium Chloride with N/5 Potassium Dichromate.*

| No. | Normality. | Original Weight. | Loss in Weight | Relative Corrosion. | Remarks. |
|---|---|---|---|---|---|
| 519 | 1/1000 | 5·9914 | 0·0018 | 60 | No visible change. |
| 520 | 1/100 | 5·9276 | 0·0282 | 940 | ,, ,, ,, |
| 521 | 1/10 | 6·0575 | 0·0713 | 2377 | Light yellow. |
| 522 | N | 6·1311 | 0·0909 | 3030 | Deep yellow. |
| 523 | 3 N | 5·9955 | 0·0987 | 3290 | ,, ,, |
| 524 | 5 N | 6·2547 | 0·1006 | 3353 | ,, ,, |

### THE EFFECT OF THE ELECTRIC CURRENT AND POTASSIUM DICHROMATE IN VARIOUS SOLUTIONS UPON AN IRON ANODE.

In order to study the behaviour of an iron anode in various solutions containing potassium dichromate and heated to a pressure of 120 to 150 lbs. per square inch, a small boiler was constructed, as shown in Fig. 16. A is a plug which screws into the top of the boiler, B. A portion of A is insulated from the rest of the apparatus by means of a porcelain arrangement similar to that found in the common spark plug. From this insulated portion an iron strip, C, can be suspended into the boiler and connected with an electric current so that it will be the anode. D is a safety-valve and E the pressure gauge. The entire boiler is so connected that it serves as the cathode.

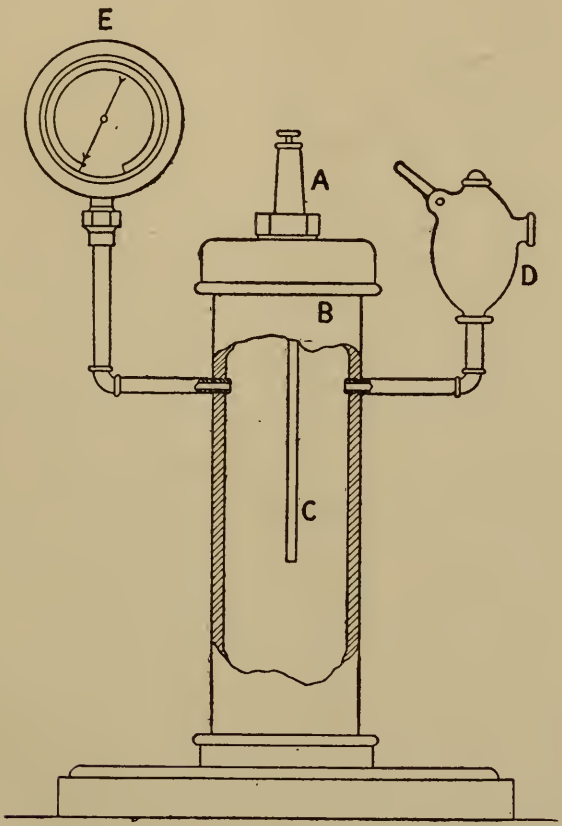

FIG. 16.

The iron strips which were used as anodes were made from commercially pure iron and had the following dimensions: 10 cm. × 0·50 cm. × 0·10 cm. The total area was 12·10 square centimetres. A small hole was drilled into the top of each strip so that it could be hooked on to A. When the plug was screwed into the top of the boiler, the iron strip would be completely covered by the solution. The hole in the strips decreased the area exposed to 11·97 square centimetres.

The boiler was heated by placing in a large paraffin bath.

N/10 solutions of sodium sulphate, sodium chloride, magnesium sulphate, and magnesium chloride were used. To these solutions potassium dichromate was added until they were also equivalent to N/10 and N/5 solutions of this substance.

In running the experiments the solutions, which would be at room temperature, were introduced into the cool boiler. The iron strip was then introduced into the solution, and the plug from which it was suspended screwed securely into the top of the boiler. The proper electrical connections were made, so that a current of two and a half amperes flowed through the system. The boiler was then immediately placed in the paraffin bath and heated rapidly until a pressure of 120 lbs. was recorded upon the gauge. At the end of half an hour the boiler was removed from the bath, and when cool enough the current was stopped and the iron strip removed. In every case it was found that the iron would be in the active condition, as a large part of it had gone in solution during the half hour treatment.

Tests were then run starting with warm solutions containing normal (147 grammes per litre) potassium dichromate in N/10 solutions of the four salts previously used. Upon repeating the experiments as described above, the same results were obtained, the increase in the amount of potassium dichromate producing no effect. A warm solution was used at the start to dissolve all the potassium dichromate.

Thus it may be concluded that the possibility of keeping iron passive under boiler conditions with the aid of an electric current and potassium dichromate is practically impossible.

## GENERAL CONCLUSIONS.

1. At atmospheric conditions the introduction of varying amounts of potassium dichromate into solutions of different concentrations of sodium sulphate, sodium chloride, magnesium sulphate and magnesium chloride, and saturated calcium sulphate, inhibit corrosion to a remarkable extent.

2. The differences in the chemical composition and physical properties of the iron and steel employed appeared to have practically no effect when placed in solutions of chlorides and sulphates containing potassium dichromate at room temperature. Differences in behaviour were noted at the temperature of boiling water.

3. At atmospheric conditions a few of the test-plates were rendered passive by the dichromate contained in certain of the more dilute solutions.

4. The rate of corrosion was reduced in some cases upon the addition of dichromate to the dilute solutions at the temperature of boiling water.

5. In N/10 and normal solutions of the chlorides and sulphates the addition of dichromate to the hot solutions was decidedly injurious to the iron and steel.

6. The commercial application of potassium dichromate to boiler waters is not practicable because of cost and uncertainty of results.

7. Di-sodium phosphate limits the rate of corrosion of the iron and steel at room temperatures when added to various solutions of sodium sulphate and sodium chloride.

8. Di-sodium phosphate does not produce the passive state when iron or steel is immersed in its solutions.

9. Slight differences in the action of the iron and steel in solutions containing di-sodium phosphate were noted.

10. Iron and steel in solutions of sodium sulphate and sodium chloride containing di-sodium phosphate and heated to the temperature of boiling water, are more readily acted upon than if the phosphate were not present. Even small amounts of this salt increase the rate of corrosion.

11. The rate of solution of zinc occurring on galvanised iron

is increased by the addition of potassium dichromate to solutions of sodium sulphate and sodium chloride.

12. Iron cannot be rendered passive under boiler conditions in N/10 solutions of chlorides and sulphates when varying amounts of potassium dichromate are added and the iron made the anode in an electric circuit.

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